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ENVIRONMENTAL ASPECTS OF CHEMICAL USE IN WELL-DRILLING OPERATIONS

(MAY 1975, HOUSTON, TEXAS)

CONFERENCE PROCEEDINGS

OFFICE OF TOXIC SUBSTANCES
ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

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16. ABSTRACT

This conference was the second in a series of three on the environmental impact of chemicals in various industrial operations.

The objective of this conference was to cover and discuss current chemical use, functions of chemicals in the operations, byproducts likely to be introduced, known health or environmental effects from chemicals used, and measures used or available for use to control environmental contamination. More specifically, papers were presented and discussions held that covered industrial emissions and effluent surveys, chemicals and their effects, reclamation and disposal and academic programs.

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21 May 1975

Opening Session

Farley Fisher, Ph.D.*
General Chairman

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*Chief, Early Warning Branch, Office of Toxic Substances, Environmental Protection Agency, Washington, D.C.

OPENING COMMENTS

Farley Fisher

Good morning to you all. I would like to welcome you to the conference on the Environmental Aspects of Chemical Use in Well-Drilling Operations sponsored by the Office of Toxic Substances of the Environmental Protection Agency, and arranged by the Research Triangle Institute for us.

I am Farley Fisher; I am chief of the Early Warning Branch of the Office of Toxic Substances of the EPA. I would also like to introduce Mr. Frank Ayer from RTI, the conference coordinator; he is largely responsible for the arrangements we have here today. Mr. Ayer and Mrs. McGuffey, his assistant, are available to assist you with any problems you may have.

In addition, before we start, I would like to introduce at least three of your session chairmen so that you will know them. James L. Lummus, Amoco Production Company, is going to be our session chairman today. Dr. C. S. Giam of Texas A & M University will serve as chairman Thursday. And Dr. Albert J. Fritsch, Center for Science in the Public Interest, will be our session chairman on Friday.

The purpose of this conference is to explore what is known about the environmental effects of the techniques and chemicals used in various types of well-drilling operations. I think that as the program develops it will be clear that the heaviest emphasis is on drilling of oil wells, but it is not our intention to neglect other types of wells; we will have some presentations on water wells and geothermal wells. And it certainly is not inappropriate for persons to raise points dealing with wells other than those--brine wells or sulfur wells, for example.

We do want to talk somewhat about the commonality of technology, and also about the distinctions in technology between various types of well-drilling operations.

I hope that we have a diversity of viewpoints represented, and I hope that everybody will feel by the time we are through that they have had an opportunity to air their views.

It is not our intention at a meeting of this type to try to resolve any of the issues which may come up, but rather merely to get them out in the

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open, so that they can be discussed further in private or in other fora, with the hope that within a relatively short period of time we may decide which are real issues and which are not, and for those that are real issues, decide exactly what can be done to help alleviate the problem.

The topics to be covered in the conference cover a very wide range. We are going to talk about well-drilling techniques that are used, and in some cases techniques which are proposed for use. We are going to talk about disposal problems with spent muds. We are going to talk about ground water contamination, which is a real bugaboo. And we are going to talk about regulatory attitudes, what kind of regulations exist now, and exactly what effect they are having, good or bad, and several other items as well.

Now, one can say, "Why in the world are you looking at this problem?" or "Why are you looking at this area? We do not think it is a problem, and, after all, the environment is in pretty good shape. The States of Texas and Oklahoma have not fallen into the sea yet, despite the fact that people said they would."

The answer to that is that we are not sure things are quite as good as we would like. You do hear stories, from time to time, about aquifers being contaminated, about vegetation being destroyed, and various other things which could or could not be a result of well-drilling practices.

There are some very serious problems of which we are only starting to become aware in a national sense, although they have been the focus of individuals' concerns for many years.

There is the question of ground water contamination, which is a very serious thing, especially from the point of view that once it has occurred there is really very little we can do to reverse it, and that there is frequently a very long lag time between the event causing the contamination and the actual appearance of the contamination.

There is the question of the disruption of marine ecosystems, which has received up to now considerably more attention than the ground water, and which is, once again, something we do not really understand very much about.

So we feel that there are very real questions. We do not know what the answers to those are and we are not pretending we know what the answers are. We hope that what transpires here in the next 3 days will bring us a little closer to those answers.

People will also say, "We are in an energy crunch. The government is supposed to be encouraging people to drill more oil wells, drill geothermal wells, and so on. You people want a brake on this whole operation." And the response to that, which I really consider to be a rather childish objection, is that we are not trying to put a brake on anything. Our concern is to see that what is done is done in as environmentally sound a manner as possible.

No matter how serious we think our current needs for oil are, they pale when compared with our ultimate need for water. And we would be making a very drastic mistake if we decided to trade off oil in the short term for water in the long term. This is the kind of mistake we simply cannot afford to make.

It might be appropriate for me to spend just a few words on what we are not intending to discuss here. We have designed this conference around the operation of drilling and installing a well. It is not our intention here to get into problems associated with accidents or improper operation of a well. In other words, we are not going to get into the subject of oil spills or gas ruptures, subjects which have been treated in considerable depth at other meetings, and of which many people are well aware. In order to concentrate on what we came here for, I would ask that we try to avoid getting sidetracked on matters of this type.

I am very happy to see you all here. I am looking forward to a very profitable and educational 3 days, and I hope you are doing the same. Success of that will depend very much on all of you feeling free to contribute what you have to contribute to the discussion as it progresses.

21 May 1975

Session I:

TECHNIQUES AND CHEMICALS USED IN WELL DRILLING

James L. Lummus*
Chairman

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*Special Research Group Supervisor of Drilling Fluids and Optimization, AMOCO Production Research, Tulsa, Oklahoma.

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SESSION INTRODUCTION

James L. Lummus,
Session Chairman

I would like to welcome you to Session I, which, as Dr. Fisher pointed out, is going to be devoted to the subject of Techniques and Chemicals Used in Well-Drilling.

Basically Session I this morning will be a discussion on the techniques of drilling, some of the various aspects of the planning and drilling and completing of wells and of some of the chemicals that are used in drilling fluids for this purpose.

This afternoon we will get into the toxicity of chemical additives in drilling muds. And I think we have a very interesting program with interesting papers.

We hope to acquaint you, the audience, and those who review the proceedings later, with some of the aspects of drilling. We hope to give you an insight into some of the problems encountered and some of the techniques and methods that are used.

I would like to make a remark basically about drilling, something that has impressed me over the years--that the drilling of a well requires the expertise of a large number of people, probably a larger number of people than most of you sitting here in the audience realize.

Today you will be hearing from people who have been involved in drilling most of their lives and who I consider competent experts in this field.

It takes both staff and operating type people to plan and drill a well. The drilling methods, new equipment, and the chemicals used in well drilling have to start with an idea, which may come from various sources. These ideas are researched by engineers and chemists in various company laboratories associated with the oil industry. Sometimes these people are unsung, but the technology to go ahead and improve drilling efficiency depends on them.

These ideas may include a new bit, or a new mud additive; they may include a new directional tool. If they are promising, they are licensed

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to service companies which, in cooperation with oil company people and drilling contractors, apply them in improving the efficiency of a well-drilling operation.

At the present time in the oil industry we have drilling costs skyrocketing. Projected costs that were made last year no longer apply. The cost to drill a wildcat well is up anywhere from 15 to 25 to even as high as 30 percent more than was projected. So it is becoming increasingly important to do a better job of planning and drilling. And it is becoming increasingly important to implement new ideas as quickly as possible. We can no longer afford the luxury of biding time with the status that we are in today.

Now, as in the case of any industry--the rubber industry, the food industry, so forth--the communication of technology, so that it can be used on a real-time basis, is one of our most difficult problems, and a problem to which we, the industry, devote a considerable amount of attention. This is evidenced by the number of technical meetings, special training courses presented at universities, seminars, and in-house training sessions by different companies that our industry supports.

One of the areas in which more dialogue is needed is the subject of this conference, Environmental Aspects of Well-Drilling Operations. Hopefully, we will be able to communicate better after today's session, which we think will be devoted to real-life situations as far as drilling wells and the possible effects on the environment are concerned.

TECHNIQUES OF DEEP WELL DRILLING

S. E. Loy, III*

Abstract

The pressing need for new petroleum reserves makes it necessary to drill to deeper and deeper horizons. The challenge of this drilling is being met by enlarged technology, improved metallurgy, and a growing skill in our crews. The capabilities and materials developed involve every aspect of the drilling process. This presentation will outline the planning and engineering that accompany the drilling of a deep well, the materials used in the operation, and the costs associated with the endeavor. Also emphasized will be the problems of temperature and pressures which place an added requirement on our metallurgy, drilling fluids, the well equipment used, and the technology of the drilling engineer.

INTRODUCTION

The drilling of deep wells is occupying a position of increased importance with present efforts to maintain an adequate energy supply. As it becomes more and more difficult to find reserves onshore at shallow depth, the deeper wells assume an increased significance. The techniques used to drill the deep well are important at this conference, though, not because most wells are deep, but because the deep well represents all aspects of the drilling procedure. This discussion will emphasize the factors that are significant in drilling the deep well; in addition, others common to all wells will be covered. The deep well, except possibly for the factor of high temperature and frequently the presence of abnormal pressure, is not basically different from the shallow well; it experiences problems and costs which are of the same kind, but on a much more severe level.

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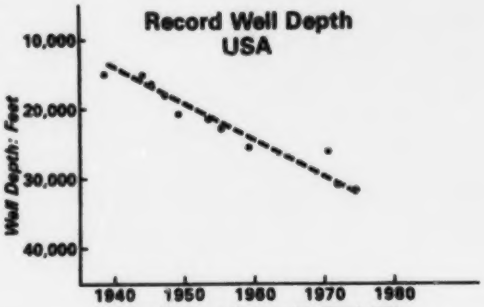
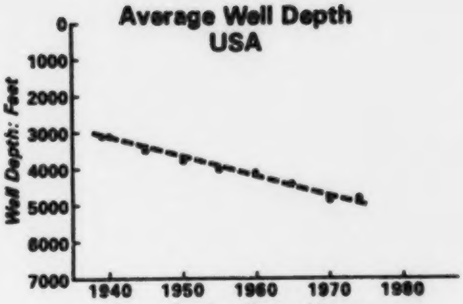
*Drilling Operations Manager, Exxon Company, Houston, Texas.



Source: Petroleum Engineer Intl. March 1974

Figure 1. Record well depth in the United States.



Source: Petroleum Facts and Figures

Figure 2. Average well depth in the United States.

Well Depths

The present trend in extreme well depth is shown in figure 1. This figure illustrates the record depths for the United States during the past 35 years. As can be seen, we, on the trend, have added almost 500 feet to the record every year. It should be noted that the depth of an average well is a much smaller number than the record depths. Average well depths are shown on figure 2. Average well depth was about 3,050 feet in 1939 and increased to about 4,700 feet in 1974. It is interesting to note this depth is only about 1/6 of the record depths. The deep well is being discussed here not because it represents the majority of the wells, but because it illustrates the majority of the drilling techniques.

THE EQUIPMENT

The rig used on a deep well must be large enough to handle strings of drill pipe and casings as much as 5 miles long--nearly 6 miles on the deepest well to date. It must have enough horsepower to hold and move the weight of this pipe in and out of the hole and to run mud pumps which circulate the drilling fluid at up to 3,000 psi surface pressure. This "mud" sometimes has a specific gravity twice that of water and is pumped at a rate of up to 12 barrels per minute. The power required for this job is usually developed

Table 1. Examples of rig equipment

	"Small"	"Medium"	"Largest"*
Mast: ft	126 (.4 million lb)	142 (1 million lb)	147 (2 million lb)
Drawworks: hp	600	1,400	4,000
Engines: hp	2--325 ea.	3--700 ea.	3--1,400 ea.
Mud pumps: hp	2--375 ea.	2--1,000 ea.	2--1,300 ea.
Substructure: ft	9	20	32

*Oil and Gas Journal, Vol. 71, No. 19 (May 7, 1973), pp. 53-55.

by diesel engines. Total horsepower on the largest land rig is near 4,000 horsepower with the average rig being near 1,000 horsepower. Examples of the basic essentials of some rigs are listed in table 1. The variation of size and type of equipment is over a wide range as can be seen from the table. The examples given indicate an approximate range. No two rigs are alike, most having been modified since construction to take advantage of new equipment or to provide capability for a specific area of operations. A large rig on location is shown in figure 3.

A drilling string used to drill at the shallower depths is shown on figure 4. Illustrated is the conductor casing (the first string of pipe set), the drill pipe, drill collars, and bit. The drill pipe is used to carry the drill collars and bit and to conduct the drilling fluid to the bit. The drill collars provide rigidity and a source of weight to the bit. The bit, of course, cuts or crushes the formation. The bit shown here is a tri-cone bit. Bit design is an important science within itself. Designs include the drag or fishtail bit, mill tooth bits, tungsten carbide insert bits, diamond bits, and many variations within these designs. Each has its own special application depending principally on the type of formation being drilled, the cost of the drilling operation, and the depth of the well.

The casing string for a deep well is illustrated on figure 5.

Figure 3. A large rig on location.

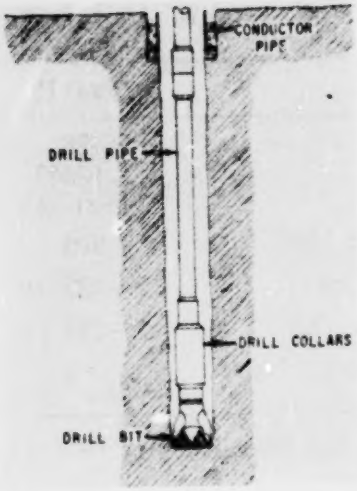


Figure 4. A drilling string used at shallower depths.

This pipe presents special problems in metallurgy. It must be strong enough in tension to hold its own weight when lengths as long as 4 to 5 miles are hung in the well. It must be strong enough in burst strength to stand the 10,000 to 15,000 psi which may be at the top of a deep gas well, and it must be strong enough in collapse to avoid crushing when formation pressures exceed internal pressures sometimes by as much as 15,000 psi. Of course, only the very deep wells experience these extreme conditions and then only a part of the string on a deep well is exposed to maximum conditions. These requirements are met by using thick well pipe and making the pipe from very strong steel. Ordinary steel used for most construction work and on shallow casing strings has a yield strength of about 40,000 psi. It is common for casing strings to use steels with 80,000 psi strengths, and some are made from steel having 110,000 psi yield strength. The highest strength steel used in casing to date is V-150 steel having a minimum yield of 150,000 psi. Steels having yield strengths as high as 135,000 psi are commonly used for drill pipe strings for deep wells. The cost of these materials requires that a high level of engineering expertise be used in the design of the string. This design is specific for the conditions of

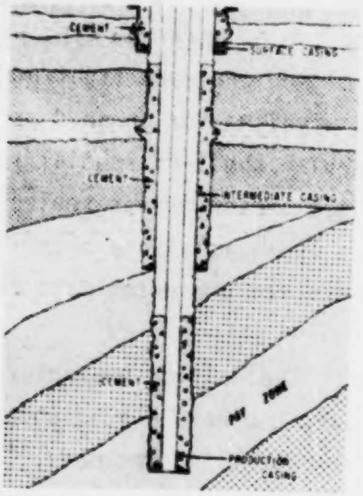


Figure 5. A casing string used for a deep well.

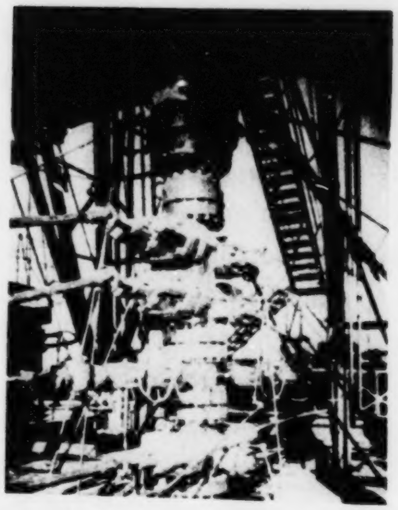


Figure 6. A blowout preventer stack for a deep well.

each deep well. In many companies, the detailed engineering calculations required are assisted by computer. The conditions to which the string is exposed and the safety factors appropriate for the particular type of use are programmed and the output specifies the most economic combinations of pipe grade, wall thickness, and connection type meeting the requirements.

The casing on a well is run for a number of purposes, among them are to protect and stabilize weak formations, to avoid loss of mud into the formation, and to protect the upper fresh water sands from possible contamination from salt water or hydrocarbons. On a deep well, a most important feature is the control of the formation pressures which may be encountered. The casing isolates the pressure and serves as the connection at the surface upon which blowout preventers can be placed for the control of accidental flow. An example of a blowout preventer stack for a deep well is shown on figure 6.

Blowout preventers are designed to be set on top of a casing string and shut off unwanted flow from the well. Two main types of preventers, the annular and the ram type, are used on a deep well. The number and arrangement of blowout preventers in the stack depends on the type and location of the well to be drilled.

Most deep wells will have one annular and two or more ram type preventers. The annular is designed to be closed pressure tight around pipe, irregular objects such as a kelly, wireline, or on an open void. The closing element is a thick annular spool of special rubber. The ram preventers are sized to close piston driven seals (rams) around the drill pipe being used. There is also a blind ram to close on an open void. One separate ram preventer must be used for each size pipe.

It is not sufficient just to close-in the well on preventers, the influx of fluid must be circulated out, the well placed under control--probably by using heavier mud--and drilling resumed. To do this requires special connections on the preventer stack, remote or manually operated chokes to hold back pressure while circulating a heavier mud to control the well, and a separator and flare system to handle any gas or oil circulated from the well. The engineering fundamentals of the well control operation are given careful attention by each drilling contractor and operating company. It is essential that their personnel be ready to take prompt and correct action so unexpected well pressure can be handled safely and without excessive expenditure.

There is always the possibility of the unexpected in any human operation, whether it is flying a jet airliner or drilling a well. In the event of a blowout, there is risk of contamination to the immediate environment. Industry continues to train its personnel and to develop its equipment to reduce this risk to a minimum. This will always be the case, for in addition to our public responsibility, the safety of our personnel and the cost of the drilling operation causes the elimination of blowouts to be a continuing prime objective in drilling technology.

The primary components of a drilling rig have been mentioned above. There is a large amount of additional equipment without which wells could not be drilled. Among these are the other components of the rig such as electric generators, shale shakers, mud tanks, degassers, desanders, desilters, auxiliary pumps, and sometimes centrifuges, power swivels, wireline units, and automatic control equipment. The equipment is selected according to the type of drilling problems expected.

DRILLING FLUIDS

The drilling fluid performs a number of essential functions on a well. Among the most important are the cooling of the bit, lifting drill cuttings to surface, maintaining sufficient pressure to hold back flow from the formations penetrated, and sealing the hole so mud or mud filtrate will not flow in significant amounts into the formation. To satisfy all these requirements, the mud must be compounded so as to have chemical and physical properties which can be carefully controlled to meet the varied and changing subsurface conditions. The science of drilling fluid control has developed to a high degree, and its application on-site is essential to the success of a well. This is particularly true of the deep well. There the high temperatures of the deep formations cause the chemicals from which the mud is compounded to react with one another or degrade at such a rate that many of the more common materials cannot be used in the deep well.

The temperature found at depth by a drilling well varies depending upon locality. The deepest well drilled to date had an estimated formation temperature of 475°F at the total depth of 31,441 feet. The highest temperature recorded in a well to date is 555°F. This well, in Southwest Texas, would have a calculated formation temperature of 590°F at 23,837 feet. Most wells have downhole temperatures much lower than these record values. The usual temperatures experienced are illustrated on figure 7. The gradient of 1.3°F per 100 feet is in the low range, whereas 2.2°F is near the upper limit under ordinary conditions. It will be noticed the temperature range for wells at average drilling depths is around 150°F.

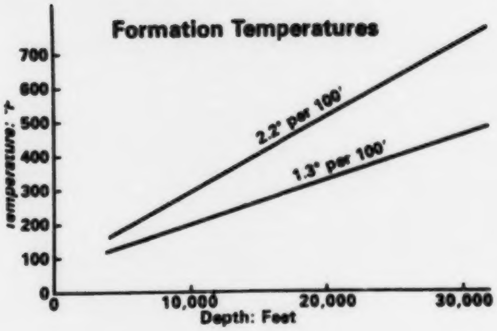


Figure 7. Formation temperatures.

Basically there are two differing types of drilling fluids: water base and oil base. Each is composed of a liquid carrying a suspending agent and a weighting agent. To these are added materials to control the flow properties of the mud and to reduce filtration into the formation. In most instances, a number of other properties such as electrolytic composition, pH, reserve alkalinity, emulsion stability, and tolerance to contamination are important. Each of these properties is important in the shallow well but a great deal more important in the deep well.

The most commonly used drilling fluids are water-base fluids. Early drilling muds were simply native clays dispersed into water. As wells got deeper and the importance of pressure control and hole cleaning became better understood, special clays such as bentonite were used, and chemicals were added to control the viscosity, or filtration rate. Also weighting agents were developed. The early viscosity control agents included tannins from quebracho and sodium phosphates. Filtration was controlled by the bentonitic clays and by starch. Weight was controlled by natural solids build-up and by the addition of inert materials, primarily barite--a natural mineral grade barium sulfate. With the exception of the barite, all these materials are susceptible to reaction and chemical change at the higher temperatures in a deep well. Though these materials are still satisfactory in shallow wells when wells are drilled deeper and temperatures approach 150°-250°F, new materials are needed. The next generation of materials was designed for roughly 200° to 300°F. Here, organic polymers such as carboxy methyl cellulose or polyacrylates are used for filter loss, and modified lignosulfonates for viscosity control. These materials are economic and perform satisfactorily to somewhere near 300°F. Past 300°F, few materials are satisfactory. Lignites are used in combination with lignosulfonates for want of the ideal material. Oil muds, discussed below, also find extensive use at the high temperatures.

Drilling fluids compounded from oil have been used successfully by the industry for many years. Besides the application in the deep wells at high temperature mentioned above, their use is important in some areas to reduce the adverse affects of water upon those productive formations which can be damaged by contact with a water-base filtrate. This was probably their first use. This application is still important, but added to it is its present application in maintaining a stable hole through formations likely to cave or slough when contacted by water and the one mentioned above--that of maintaining a mud system satisfactorily tolerant to very high temperatures. Also the oil phase mud has found wide use in avoiding stuck pipe in difficult holes or as spotting fluid for freeing pipe once it has become stuck. These uses make oil muds important to everyday drilling, and extremely important to deep drilling.

The composition of oil muds vary over almost as wide a range as do water base muds. Generally they have a composition whose components perform in the oil carrier the same functions that are performed by their counterparts in a water base composition. Oil muds are to be reviewed in detail in a discussion to follow. A very brief list of their components would include bentone clays, asphalts, electrolytes, water (in emulsion), and organic agents designed to thin the composition or stabilize the emulsion.

ABNORMAL PRESSURE

The technology of drilling the deep well has been covered to a degree during mention of metallurgy, equipment, and drilling fluids. However, there is one special subject which bears discussion. This is the detection and control of abnormal pressure.

Normal pressure is defined as the subsurface pressure resulting from the column of water naturally present in the formations from the surface to a specific depth. This water is usually salt water, but it can be fresh. Abnormal pressure then would be pressure in excess of this value.

Abnormal pressure does not occur at all in some areas. In areas where it does occur, it is erratic so one can speak only in trends. The following examples are given as illustrations. In Central Mississippi, abnormal pressure occasionally is found somewhere below 20,000 feet. Inshore along the Texas and Louisiana Gulf Coast, it often occurs at between 9,000 and 11,000 feet. Offshore in the Gulf of Mexico, the point of abnormal pressure occurrence becomes shallower as one goes away from the coast with abnormal pressure occurring as shallow as 4,000 or 5,000 feet in the deep water some distance offshore. In other areas of the country, its occurrence is likewise spotty.

The detection and proper handling of abnormal pressure is essential for the successful drilling of any deep well. First, the mud weight and casing program for the well is planned to provide mud weight and/or casing at the proper depth to control the formation pressures. The casing cannot be set arbitrarily early because the formations higher up the hole will break down and cause loss of drilling mud as higher mud weights are required to control higher formation pressures. On the other hand, if an attempt is made to set casing too

Table 2. Abnormal pressure indicators

A.	Increased:	Drilling rate Mud gas Mud chlorides Mud temperatures
B.	Decreased:	Sonic velocity Shale resistivity Shale density
C.	Appearance of shale	
D.	Micro fauna in shale	

deep, then the well may "kick" because the mud weight is too light to hold back the formation pressure. The well will still be controlled by blowout preventers, but their use should be reserved only for emergencies. The proper placing of each string of casing in an abnormal pressure well then is critical and must be tailored to the actual downhole conditions.

Abnormal pressure can be predicted before a well is drilled through use of seismic data and by knowledge from previous wells. As the well is being drilled, there are a number of important indicators which are used to detect imminent abnormal pressure occurrence. Table 2 illustrates these indicators. Among the more common ones are sudden increase in drilling rate, increased gas in mud, increased chlorides in mud, increased mud temperatures, decreased density of shale cuttings, reduced electrical resistivity of shales, reduced sonic velocity of shale intervals, and the physical appearance of the cuttings. Also the micro fauna contained in the shale cuttings is used as an indicator. These techniques are under continued research and development. An important part of the job of drilling personnel is to work with their improvement and application. An example mud weight and casing program for an abnormal pressure well is shown on figure 8. These casing and liner strings are costly and cannot be

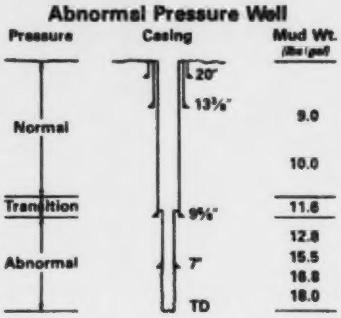

Abnormal Pressure Well
Pressure
Casing
Mud Wt. (lbs/gal)
20"
13⅜"
9.0
Normal
10.0
Transition
11.6
9⅝"
12.8
Abnormal
7"
15.5
16.8
18.0
TD

Figure 8. Abnormal pressure well.

run arbitrarily; but often, even more critical, there is a limit on how many can be run because each must have a smaller diameter than the previous one used. A well can simply run out of room to set another string of casing if the planning and execution is in error.

The deep, abnormal pressure well can be drilled successfully. The plans that go into such a well are much more detailed than those for the average well, and the application of proper technology assumes critical importance; but the job can be done. The industry will continue to improve its techniques and meet this challenge.

CONCLUSIONS

1. Our search for new energy will require the industry to continue the trend toward drilling deeper wells.
2. The drilling equipment increases in size and technological complexity as wells are drilled deeper.
3. The challenge of drilling the deep well is being met by industry technology.

DISCUSSION

MR. RICHARD S. SCALAN (University of Texas, Port Aransas, Texas): You mentioned use of cement casings, and so on. Is there something in drilling wells, in general--in deep wells in particular--perhaps additives, that might be in the cement, that might be of concern in the protection of the environment?

MR. LOY: Cement is, of course, used in a manner such that the formation is subjected primarily to filtrate, which is basically just water. And certainly there are some retarding agents that might go with the water to penetrate the formation to a very limited extent. But the penetration of this water filtrate into the formation is just a matter of a few inches, since not very much of it is placed around the casing. So its impact within the boreholes would be very minor if significant at all.

As far as the additives that go into the cement possibly being of concern, I really cannot answer. Maybe somebody here can. I do not think there is anything basically harmful.

Now, certainly, cement has been used in the construction industry for many years. The type of cement that we are using to cement the conductor and surface casing strings is not basically different from that which has been used in the industry.

Any excess cement that is circulated out is generally disposed of such that it is not a deterrent to life.

DR. PAT M. WENNEKENS (Alaska Department of Fish and Game, Anchorage, Alaska): There seems to be a trend in your graph showing so-called abnormal pressure as you go further offshore. As you go more toward the continental slope, do you expect these trends to proceed the same way? Also, do you have any comments on what was observed during some of the deep drilling done by the Glomar Challenger in the Gulf of Mexico, in terms of unusual pressures when they went to the deeper water depths?

MR. LOY: I can answer the second question first. I am not really acquainted with what the Challenger encountered, but I am acquainted with the limited information we have of deep water in the Gulf of Mexico as well as of the shallow water. I can say that it would appear that maybe there could be some trend to having abnormal pressure occurrence at a shallower depth as you get into deeper water in the Gulf of Mexico. The occurrence of abnormal pressure is spotty and erratic, as I mentioned in my talk here, you can only speak in trends. You would have to know a particular area to isolate where abnormal pressure might be encountered in that area.

CHAIRMAN LUMMUS: You might add, the more shallow it is, the more dangerous it is for well drilling.

MR. LOY: That is true. Of course, the shallower this abnormal pressure occurs, the more you are limited on the hydrostatic head of the drilling mud that can be placed.

DR. WENNEKENS: Some hydrocarbons were shown Sigsbee deep in the Gulf, and I was wondering if there was any evidence of a pressure problem in those readings. Can anybody in the audience comment on that?

MR. WILLIAM DOLLINGER (Sherwin-Williams Company, Houston, Texas): We are concerned with chemical use in well-drilling operations. In your slides you showed emulsifiers, and you showed surfactants. You did not mention corrosion inhibitors. I wonder if that was intentional or otherwise?

MR. LOY: No, it was not intentional. I could have mentioned a lot of control inhibitors, and they certainly can be a vital part of the drilling fluid, depending on the conditions which you encounter.

CHAIRMAN LUMMUS: I think Sam was tripping around a little bit because he did not want to say everything that Jay Simpson is going to say later about drilling fluids and what Mr. Braunlich is going to say about completion and other techniques later on. It was just kind of an outline of the drilling operations. We are going to discuss some of the more specific chemicals a little later on.

MR. JAMES W. WINFREY (Petroleum Consultant, Houston, Texas): Sam, I think it would be worthwhile for you to say a little bit about the problem of lost returns. You did not say why you set this intermediate string of casing. Some of these people may not understand it. That is a part of the drilling technology.

MR. LOY: I did mention it, but I did go rather rapidly.

The intermediate casing string is used to protect the weaker formations. As you go deeper, you need to carry heavier mud weights. Of course, the shallower formations tend to break down and you tend to lose circulation, as we term it, or lose the drilling fluid into the formation. That is the reason for the intermediate casing string.

The big problem in drilling deep wells is that you tend to run out of casing strings. If you are drilling rather deep, you will have to start with a large size of casing in order to have enough string to reach your objective, because you have weaker zones that you have got to protect--first of all, shallow water, fresh water. You need to protect the weaker zones from breaking down. And then, of course, you want to keep abnormal pressure fluid from coming into the well. Then you may even have a reversion back to normal pressure below that and have to set another string to get to the objective. This is one of the tremendous costs that go into deep well drilling.

TECHNIQUES OF SHALLOW WELL DRILLING

Robert R. Peters, P.E.*

Abstract

The various methods of drilling for the construction of water wells began with the cable tool machine and since have advanced up to rotary, reverse circulation, and air drilling. The very beginning of water well drilling by the utilization of cable tool machines dates back to approximately 600 B.C. Since then many innovations have been incorporated. The orderly development of ground water is a major responsibility of water supply contractors. It is necessary that construction be such that this vast resource not be destroyed. In recent years, we have found that increased sophistication and methods of construction present problems to the environment. The disposal of construction clays and/or chemicals utilized in the development of water supplies is presenting increased problems. The methods and/or disposal sites will require careful investigation.

The various major methods of drilling are the cable tool, standard mud rotary, reverse circulation, and air drilling.

The cable tool, or percussion method, is the oldest system in history and dates back to the first recorded wells drilled by this method in China, about 600 B.C. These early wells were drilled a few hundred feet deep. By A.D. 1500, holes were being drilled to depths of 2,000 feet. After the completion of the Drake oil well in 1859, many advances were made in this method of drilling. It today is used in many instances of hard rock, or cavernous drilling, but it is a rather slow

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method whereby a string of tools are lifted and dropped to break up the formation. The tools then are removed and a bailer installed to bring the cuttings out of the well. In unconsolidated formations, it is necessary to drive pipe as the drilling progresses. In some instances, water and muds have to be added in order to get the cuttings out of the hole.

The early history of rotary drilling indicates that it was used by the early Egyptians quarrying stone for the pyramids. The earliest use of the method of rotary drilling as practiced today, using hollow drill rods and circulating fluids to remove the cuttings, was by an English patent issued to Robert Beart in 1844. Since that time many additional patents have been issued for various methods of rotary drilling. However, the rotary method became commonplace after 1901 when Captain Lucas drilled the spindle-top discovery well near Beaumont, Texas, using rotary tools. Today, approximately 90 percent of the wells are drilled using this method or some combination thereof, depending upon the formations encountered.

As to the use of drilling fluids to increase viscosity, the first step, especially in the water well business, was to locate the local clay banks whereby native clays were used to prevent circulation loss, keep the bit cool, and remove the cuttings from the hole. Today our methods and fluids used are much more sophisticated, and we have the ability not only to control the weight of the fluid, but its viscosity and sand content. Today a mud engineer is available on large wells to be certain that the fluid is kept in proper condition at all times. In the water well business this service is limited and is normally performed by the driller on site, using tools or apparatus such as marsh funnel, sand content indicators, and pH paper together with mud-weighing equipment.

We, in some circumstances, utilize various clays such as bentonites, native clays, starches, and gum products. The greatest number of our wells drilled in alluvial materials are done by the utilization of bentonite fluids. We do, however, in conditions of drilling into salt water formations, use starch products. Gum products, which are biodegradeable, are also used for formation drillings. In other words, the well is made down to the top of the formations, and a changeover to gum products for the purpose of cutting the formation is used. This material has a time life and, unless expelled, degrades itself biologically. It has, upon occasion, generated some problems with bacteria being produced from the well after development. This normally is controlled by chlorination to eliminate this problem.

We are required, under some circumstances, to use various weighting agents due to higher formation pressures. However, it is our normal procedure to maintain as low a mud-weight-to-water ratio as possible. In the development of formations with low static water levels, the higher mud weights create considerable pressure on the face of the formation and cause deeper mud penetration, which is a problem in the development of the well itself. The method of reverse circulation drilling is the opposite of straight rotary whereby the cuttings are brought back up the drill pipe rather than floating up the bore hole. This allows much reduced mud use due to a constant velocity maintained inside the drill pipe. It is employed at times with combination machines that are capable of both straight mud rotary and/or reverse circulation drilling. It is limited in depth capabilities due to friction loss in pipe. This capability bas been increased in recent years due to the addition of air lift principles to bring out the fluids.

The air rotary method using a hammer is very effective in the drilling of hard rock formations. It is practically replacing the cable tool machine due to its very rapid rate of penetration. Air is pumped through the drill pipe down to the bottom where a percussion hammer is operated, breaking up the formation by the rapid reciprocating movement of the bit. Foam is sometimes used with this method to increase this capability.

Let us look first at a deep water system design and see what has to be done to build an economical and practical well water supply. Many areas of our country are blessed with excellent quality subsurface water at relatively shallow depths. This makes it easy to build a system if a good water supply contractor is available in the area. He would normally be contacted by an engineering firm or municipality and asked to assist in the writing of specifications, or to negotiate directly. Here is where the major responsibility begins and must be assumed. We can and must accept this responsibility if our industry is to survive and prosper. This most probably will be challenged, as our industry has survived many centuries; however, we must continue to improve and move enthusiastically into the 21st century. Self-policing and proper direction will enable our industry to gain the respect and confidence it so rightly deserves. If we do not police ourselves, someone else will do it for us. An example of this is the recent water laws being enacted in many States, together with sometimes stringent requirements for well permits. More and more regulations will be enacted, and therefore we must play an important part in seeing that these rules and regulations are properly drafted.

In order to properly put into perspective the advantages and economics of a ground water system, it is important to know something about surface water supplies and their respective advantages and disadvantages. We should be in a position to point these out in our discussions with our customers. It also is imperative that we carefully explain how and where ground water occurs, remembering that it being out of sight automatically causes it to be shrouded in mystery. However, there is no great mystery about ground water, only superstition caused by lack of knowledge of the unknown. We in this field are blessed with the ability to understand its occurrence. Our role then is to convey this understanding to our customers and not allow unqualified people to continue in the furtherance of superstition and false information.

Whether called in by the municipality either through their engineers or by our own investigation, the responsibility of developing the very best system that is practical is our goal and duty. Here is where we must display our best professionalism. If we are working with systems which have been in existence for considerable time and this is only an extension, then our role is to see that the original design, if proper, is continued and nothing is done to alter or reduce the dependability of such a system. This is where careful investigation of the original system is important. We would locate on a map the site of each well, check the distance that wells are apart, and check whether we are beginning to box in the wells that are causing excessive drawdown. This, as you know, costs the customer many extra dollars due to pumping costs.

Be informed on new developments in the area. Check with the U.S. Geological Survey and State Water Agencies as to investigations and recent reports. Water levels from past records should be compared with records of recent investigations. If during these preliminary investigations you find data which indicate potential problems, this is where you should recommend that a professional ground water consultant be called to evaluate and confirm your data. Many ground water systems have just grown and lacked proper planning for the future. This, when very little water was being taken from an area, caused no apparent problems. However, if our resource is to be developed to its potential, we must use all the tools available in order that we do not destroy an aquifer for future use.

Are we developing the best quality water that a given area has available? Here is where preliminary research should be conducted, and if it is not available, a testing program should be initiated to secure this information. The best quality water available should be developed for the customer. Only when these things are done on each and every job are we ground water developers. This is the way to prevent the loss of a ground water customer to a surface supply.

Old systems for many reasons have been improperly designed and developed. There is no excuse in today's modern technological world, with the knowledge and equipment that we possess, for improper design and development. Let us carefully evaluate our position and begin the development of a complete new water system. In the beginning, all of our preliminary work is the guiding of design criteria in the advantages of using a ground water system. This sounds relatively simple, however, being able to look out on a vast reservoir or lake with its esthetic values has considerable appeal to many water users. The vast water treatment plant required for these systems is quite a monument to the engineers or city fathers for many years to come. The potential recreational opportunities sometimes afforded are also a selling point. The well with its accompanying pump head and electric motor sitting on top is a small item and yet is the only visible sign of considerable money that has been spent.

Now what do we have for our ground water system? This really is rather basic, but has quite an appeal, and that is economics. The cost of surface versus ground water is on the order of 15 cents versus 5 cents to produce. The original capital investment of a surface versus a ground water system can be on the order of ten to one. Step number one will cause most to listen. Next is dependability, and here is where we meet the test. This is where we must be able to sell the unseen. This also is where we fight such quotes as "The well has gone dry," "vein of water," and "water witching."

Many major industries and cities such as Berlin, Paris, Memphis, and Houston depend upon or are largely supplemented by ground water supplies. Understanding the basic hydrological cycle tells us that ground water has been and will continue to be a vast resource of fresh water for our future needs. Our problem then is to unveil its secrecy and to convince the customer that the dependability of deep water is as good as or better than a surface supply. We have practically eliminated the evapotranspiration problems and have a source protected from contamination, this only being as long as we use proper techniques and design. In many instances the quality is such that we can pump directly from the well into the mains. A well equipped with vertical turbine pump and electric motor producing one million gallons per day is a far cry from a pumping station and treatment plant of the same capacity.

If we are requested to assist in the development of a ground water supply, what now is our responsibility and role? Our first job would be to present the customer with all of the available information that we have on the area. This could very well be a supplement to a surface water supply, due to limited production from a surface area. Existing records of nearby wells which would give information to effectively produce a dependable water supply would be analyzed. State agencies and the Geological Survey would be contacted for data on wells in the area. Sometimes it may be necessary to extend and cross-section this data with information from areas on either side. It is very probable that some wells have been developed and information is available as to the quality of ground water in the area. This would certainly be the type of information that we would want to present to the engineer or customer. From these records, we would also be able to partially determine the availability of the ground water supply and whether or not it could be pumped to the capacity requested. If treatment was necessary in outlying areas, it very possibly would be necesary in the area of investigation. Some assumption would have to be made as to the production of a particular unit and also a general idea of spacing, depending upon information from other nearby sources. Once this basic information was available, a potential well design could be drafted. This would allow for certain sizes of casing due to the pumping capabilities of the aquifer and also water levels and thickness of formations. It would be at this point that a recommended test program should be employed to actually determine the productive capabilities of the aquifers, also the aquifers that would be eliminated due to the quality of the water and the formation productivity. We certainly would want to produce for the customer the best quality of water available in the area. This would reduce his cost and also eliminate maintenance for the future.

Assumptions would have to be made as to potential yields; however, upon drilling the test hole and securing this data, a test well would be installed to collect hydraulic information on the aquifer. It may be necessary to put in several observation holes and conduct pumping tests to ascertain this information. Once this data was secured, it would then be a matter of designing a system to give the customer a safe and dependable water supply for the future. It should be pointed out very carefully that the well design and construction must be such to give a safe and dependable supply for the future, to protect for the future, to protect for the lowering of water levels, and to positively prevent the contamination of the aquifer that we are developing. All systems should have surface casing sealed and cemented to the top of the water-bearing aquifer. This would be done by pressure cementing and is the finest insurance that the customer could have. The drilling contractor that fails in this endeavor is not only destroying the aquifer as a productive source, but when this is done, has destroyed himself by having no resource to develop. It is the duty and responsibility of the well-drilling contractor to design a well to be the most economical and not necessarily the cheapest.

Many ground water customers have been lost to surface water supplies due to poorly designed and improperly constructed wells. This also is where engineers have been put in a position of embarrassment because of water supply contractors using improper methods and materials Their failures in this endeavor have caused engineers to be very skeptical about recommending ground water supplies in the future. We should never allow ourselves to be talked into any design that we feel is not safe and adequate. It is quite possible at this point that we would acquire a customer, but this would be a short-term loan, and the penalties would be great indeed. Casing size and thickness should always be ample to allow easy installation of pumping equipment and not having casing failures because of improper wall thickness. Screens, if used, should be of corrosion-resistant material that will enable long and dependable service. Means of access into the wells should be provided that will allow water level measurements and other investigations which would be conducted in the future. It must be emphasized that all well designs should be to safe yields and not beyond. We should not cause excessively low water levels because of overpumping a particular well. Well experience and hydraulics should be given careful consideration at this point. Excessively low water levels generate many rumors; if these can be averted, they should be. However, improper design of many small systems will trigger problems, because of large municipal and/or industrial developments in an area. Wells that have this problem are usually designed prior to any large ground water withdrawals in an area. Here again is where the water supply contractor has to explain what is happening in an area. This sometimes is very hard to do when an individual has lost a sizable investment because of improper design. In the future, we must prevent this from happening.

We should offer to the customer all the advantages of our technological research and skill. This means that all new techniques should be applied to each and every job. There are many instances when specialized problems are involved, and this is where they should receive specialized treatment. A few of these to receive consideration and mention would be programs such as electric analog and digital computers; these techniques are extremely valuable in analyzing such problems as excessive low water levels, possible salt water encroachment, and such things as water quality change. Pumping water from any area causes flow net changes, and if an area should have undesirable waters that are affected by a particular flow net, this water could be moved into our area of pumpage. This type of investigation is also extremely valuable when the area of pumping would be subjected to possible salt water intrusion or encroachment. These are the things that can be forecast ahead of time by the use of electric analogs and other tools of this nature.

Development of large capacity wells begins with the drilling of a pilot hole to the full expected depth of the well. Previous data in the area would give us information as to what this depth would be. Samples are taken at approximately every 10 feet and at each change in formation. These samples are analyzed and sieve analysis run to determine screen size and/or gravel size, if same is to be utilized. We then would proceed with conducting geophysical logs, obtaining resistivity self-potential, gamma, etc., to ascertain exact locations of screens to be set opposite water-bearing formations. These data, together with information on other wells in the area, would enable us to design the permanent construction of the well. If, however, water quality is a factor, it may be necessary to build miniature wells and actually pump formation samples for analysis. The final design of the well having been ascertained, we then would proceed to cut a large diameter hole to receive the surface casing. This casing would normally be set to the top of the water-bearing formation or formations to be developed. A cememting procedure would then be conducted to fill the annular space between the casing and the bore hole completely back to the surface. After the cement has set, a hole of approximately the inside diameter of the surface casing would be drilled to the bottom of the water-bearing formation. It may be necessary now to enlarge this hole by the use of underreaming tools to a much larger diameter. Careful mud control at this point is very important. The screen line itself is then installed, together with connecting lengths of pipe to either extend up inside the surface casing a depth of approximately 50 feet or return completely to the surface. If a lap joint is made up into the surface casing, a method of backing off by the use of right/left couplings would be employed and screen line normally would be hung with the use of the drill pipe.

If the large diameter well method is employed, a conductor pipe for the purpose of pumping gravel would be used to fill the annulars between the screen line and the formation's face. This area is completely filled and the gravel is extended up inside the surface casing a previously determined amount or brought completely to the surface. When this gravelling operation is completed, the well would normally be flushed with clear water and developed (see figure 1).

The development method would vary, depending upon several circumstances. There are times when air pumping and swabbing would be employed as in the construction of multiple screen wells. The development at times presents problems due to formations of higher permeability developing faster with the lower permeability formations pumping little or no water. Once the development of the well is complete, a test pump is installed to ascertain the production capacity of the aquifer. Once basic preliminary water levels are established, a pumping test would be conducted to ascertain the production capability, transmissivity, and area of influence of this particular well, or, in the case of several, the well field itself.

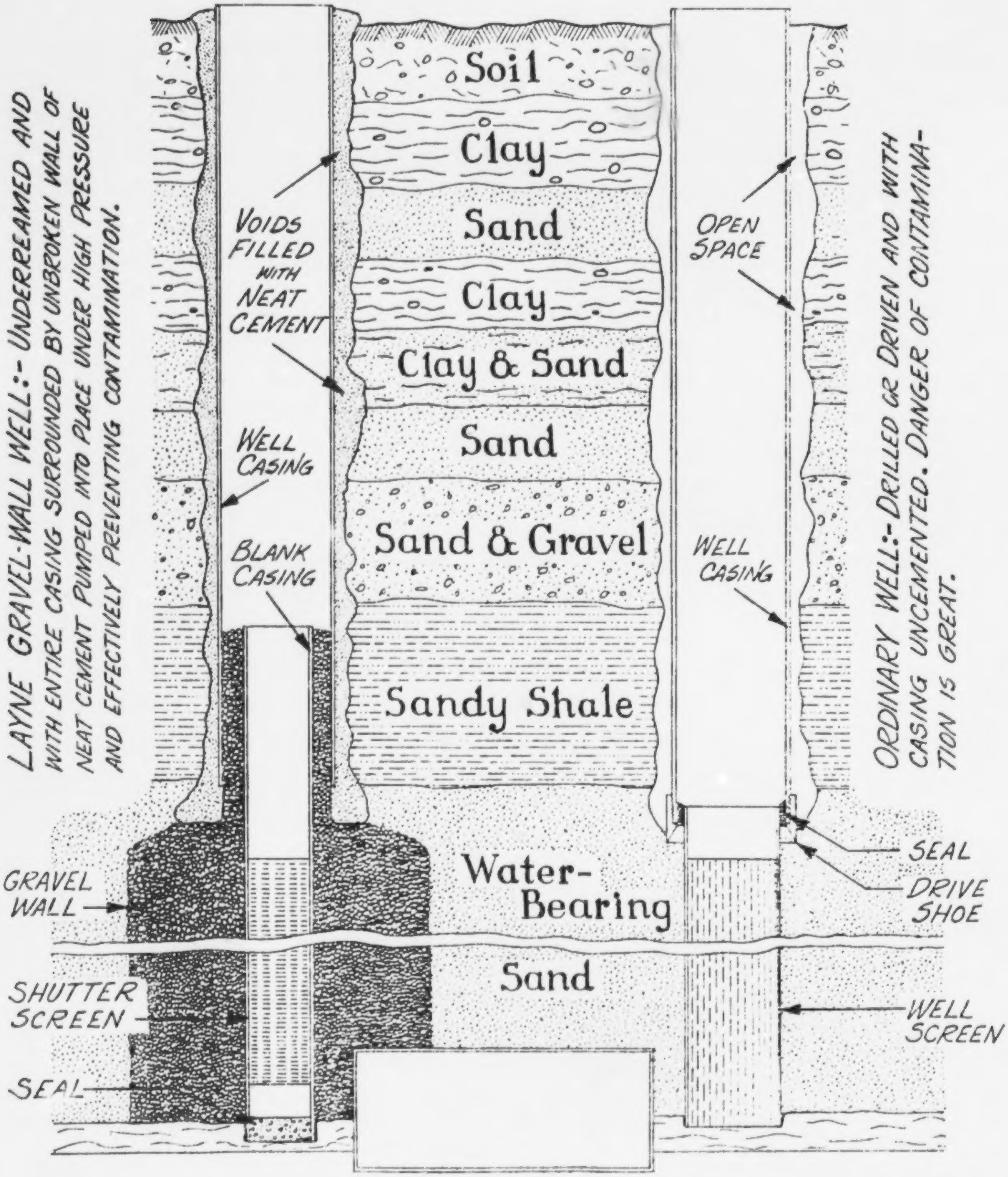
LAYNE GRAVEL-WALL WELL:- UNDERREAMED AND WITH ENTIRE CASING SURROUNDED BY UNBROKEN WALL OF NEAT CEMENT PUMPED INTO PLACE UNDER HIGH PRESSURE AND EFFECTIVELY PREVENTING CONTAMINATION.
Soil
Clay
Sand
Clay
Clay & Sand
Sand
Sand & Gravel
Sandy Shale
Water-Bearing
Sand
VOIDS FILLED WITH NEAT CEMENT
WELL CASING
BLANK CASING
GRAVEL WALL
SHUTTER SCREEN
SEAL
OPEN SPACE
WELL CASING
SEAL
DRIVE SHOE
WELL SCREEN
ORDINARY WELL:- DRILLED OR DRIVEN AND WITH CASING UNCEMENTED. DANGER OF CONTAMINATION IS GREAT.

Figure 1. Cross section showing superiority of a Layne underreamed gravel-wall well with casing cemented, over an ordinary gravelled or ungravelled well with casing uncemented.

We have found in recent years a considerable increase in the sophistication and techniques of developing large production water supplies that are dependable over many years. We have encountered considerable difficulty at times due to a lack of knowledge of our business in the normal engineering profession. It is a lot easier for an engineer to look at a lake and see a water supply than it is for him to ingest in his mind the potential of underground aquifers.

We are also having problems at the present time with the possible contamination of some very prolific aquifers due to poor construction methods which cause leakage, and/or to improperly constructed injection wells. From an environmental standpoint, one recent example is a situation that occurred on one of our jobs presently under construction whereby we were told and on the plans were shown the area for the disposal of the water from the well. Our normal assumption would be that this included dirty water, being mud, and clean water from the final test pumping. We would expect drill cuttings as such collected in the pit would have to be removed and disposed of elsewhere. We found, however, that we were not going to be allowed to put the water in a small drainage stream on one site and a storm sewer on another due to the fact that the water contained considerable turbidity. This problem has been resolved at the present time by pumping this fluid to a sanitary sewer approximately 1,200 feet from the drilling site. It was pointed out to us that it was our responsibility to dispose of this fluid. Our reply was, "Where?" No one had an answer except that it was our responsibility. Fortunately we were working for a governmental agency which in turn was dealing with a governmental agency. Had this been private enterprise, we probably would still be trying to resolve the problem. We must immediately take the necessary steps that allow us to face this problem before a contract is signed, not after.

SOLUTIONS FOR SOME PROBLEMS RESULTING FROM REFREEZING OF PERMAFROST AROUND A WELLBORE*

T. K. Perkins, G. R. Wooley,
and F. W. Ng

Presented by C. R. Knowles †

Abstract

New well completion technology has been developed to deal with problems unique to Arctic permafrost areas. During drilling, completion, and production, some thawing of permafrost around the wellbore occurs. If wells are not produced immediately after completion, or if production is interrupted at a later time, the thawed region around the wellbore will begin to refreeze.

Refreezing of the permafrost can lead to two types of problems. First, as water in the thawed region is converted to ice, its volume increases. This results in high fluid pressures which are imposed on the outer casing. Full-scale field tests, extensive laboratory measurements of the mechanical and thermal behavior of permafrost, and theoretical and computer studies have led to an understanding of these pressures. External refreezing pressures calculated for normal operating conditions are in a range that can be tolerated if the proper casing is selected.

A second potential problem is the refreezing of fluid within the wellbore system itself. If freezable fluids are left in annuli during the completion process, the possibility of high internal pressure exists. Because of the low pipe expansibility, pressures can rise to values which will cause collapse of inner strings or burst of outer strings. There are several practical approaches to avoiding this potential problem. This paper describes a unique displacement process which has been used to replace freezable fluids with nonfreezable, thermally insulating casing fluid.

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†District Drilling Engineer, Atlantic Richfield Company, Production Research Center, Plano, Texas.

INTRODUCTION

The discovery of oil in arctic areas has led to significant changes in drilling and well-completion practices. The harsh winter environment has necessitated substantial changes in surface operations. In a less obvious way, subfreezing temperatures have also created subsurface problems of considerable significance. The subsurface problems considered in this paper result from the interaction of permafrost with the wellbore.

Permafrost of various thicknesses occurs in Arctic regions where commercially significant hydrocarbon reserves may be found. Many wells have now been drilled and completed on the Alaskan North Slope where approximately 2,000 feet of permafrost are encountered. Even thicker permafrost has been reported in Russian technical literature. During the drilling and well-completion operation, some thawing of the permafrost is caused by the drilling mud which brings heat up from the earth below the permafrost horizon. Drilling can typically result in a thawed region of a few feet in radius. Production of hot oil for a long period of time can lead to thaw radii of several tens of feet (refs. 1,2,3), the exact value depending on the operating conditions and the degree of wellbore insulation provided in the permafrost region. If the wells are not produced immediately after completion, or if production is interrupted at a later time, the thawed region around the wellbore will begin to refreeze.

Refreezing of the permafrost can lead to two types of problems. First, as water in the thawed region is converted to ice, its volume increases. The increasing volume leads to an increase in fluid pressure which is imposed on the outer casing. The wellbore must be designed to withstand these "freezeback" pressures.

A second potential problem is the refreezing of fluid within the wellbore system itself. If freezable fluids are left in the annuli during the completion process, the possibility of high internal pressures exists due to the volume increase accompanying freezing. Because of low pipe expansibility, pressures can rise to values which will cause collapse of inner strings.

This paper describes some practical solutions to these two potential problems.

EXTERNAL FREEZEBACK

Consider first the external freezeback pressures. As the permafrost region around a wellbore is heated, ice in the soil pore space thaws and its volume is thereby reduced approximately 9 percent. A pressure decline resulting from the volume decrease tends to be limited by gas expansion or influx of fluid such as drilling fluid filtrate, water from a thawed region near the surface or below the permafrost, laterally flowing brine, and gravity flow from thawed sections above. Permafrost refreezes most rapidly near the surface; hence, excess water may be trapped when deeper thawed regions refreeze. Upon refreezing, the water in the pore space expands, thus tending to increase the pore pressure. The increased pressure may simply force fluid to flow to another region. However, if this is not possible, the pressure continues to rise until the soil or well casing deflects or yields sufficiently to accommodate the excess volume.

Freezeback pressures have been studied in full-scale field tests at Prudhoe Bay (ref. 4). Two wells were drilled and completed through permafrost to investigate thawing and refreezing phenomena. Thermistors and pressure transducers were attached to cables which were external to the casing. Thawing was accomplished by circulating hot fluid in the wellbore. During the thawing and subsequent refreezing cycles, temperatures and pressures were recorded at the surface.

The Drill Site 4-6 was spudded February 14, 1972. A 20-inch conductor pipe was set at 109 feet RKB, and a 17-1/2-inch hole was drilled to 2,700 feet with fresh water mud. A 13-3/8-inch, 72 lb, N-80 modified buttress casing, with external instrument cables was run to a depth of 2,191 feet. The first stage of cement was 700 sacks of Permafrost II with the top identified at 1,580 feet with a cement bond log. The second stage was cemented with 400 sacks through a DV tool at 486 feet. The 20-inch by 13-3/8-inch annulus was displaced with an oil-base casing pack, and the well was completed with open-ended 3-1/2-inch 9.2 lb, N-80 buttress threaded tubing hung at 2,044 feet.

The second well, Drill Site 1-6, was spudded May 27, 1972. An 18-1/2-inch hole was drilled with oil-base mud to 2,750 feet. The well was completed with 20-inch conductor set at 107 feet, 13-3/8-inch landed at 2,698 feet, and 3-1/2-inch tubing perforated at the bottom and hung at 2,544 feet. The bottom of the 13-3/8-inch casing was cemented with 1,350 sacks of Permafrost II cement in one stage.

The fluid circulation system for the two wells consisted of direct-fired oil heaters, circulation pumps, temperature controls, flow meters, and temperature and pressure recorders. The circulating fluid was a 50-percent mixture of ethylene glycol and water. The heat flux of 1 to 1-1/2 MM Btu/hour for thawing was produced by fluid flow rates of 2 to 3 BPM.

Several thaw-and-freezeback cycles have been completed in each well. A summary of thaw cycle data is presented in table 1. The first cycles in both wells were designed to simulate heat transfer to the permafrost during the drilling and completion of a development well in the Prudhoe Bay Field. The second cycles represent heat transfer to the permafrost during short production periods for a normal producing well. Circulation in one of these wells for one month would transfer heat to the permafrost equivalent to many months of production since the production wells will be completed with materials in the wellbore that provide greater insulation. Later cycles were made in the wells to investigate the effects of multiple thaw-and-refreezing and of changing the thaw radius.

Temperatures external to the casing were recorded each 6 hours during both the thaw and refreezing parts of each cycle. Several additional temperature surveys were run in each well using a precision wireline instrument. Within a few days after circulation was

Table 1. A summary of thaw cycles

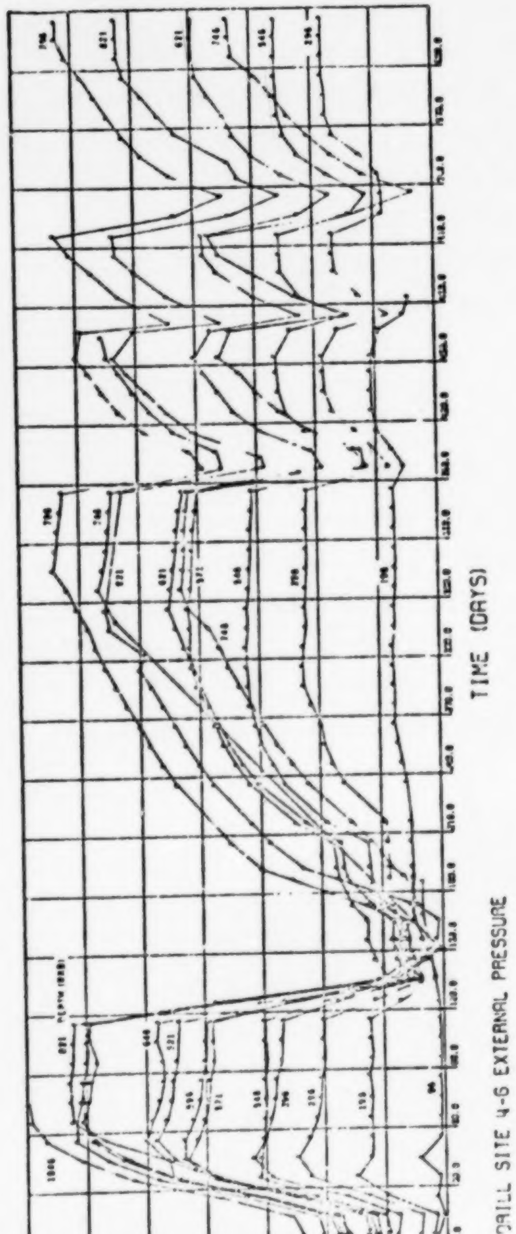
Well & cycle no.	Date at beginning of thaw cycle	Time at beginning of thaw cycle measured from beginning of first thaw cycle, days	Average input fluid temp. °F	Circulation rate, BPM	Circulation time, days
D.S. 4-6					
1	2/22/72	0	113	12.4 (Rig pumps)	7
2	6/28/72	126	160	2	32
3	3/17/73	389	140	2	7
4	6/4/73	468	130	2	3
5	7/27/73	521	135	2	8
D.S. 1-6					
1	6/9/72	0	138	3 (Reverse)	7
2	9/17/72	201	150	3	10.5
3	3/7/73	373	125	3	90

stopped, the temperatures throughout the monitored sections of the wells dropped to the freezing point. The depth at which total freezeback had occurred was indicated when the temperature would start dropping below the freezing point, which depends on water salinity, pressure, lithology, and mineralogy. This freezeback depth progressed down the hole as water in the formation and, in Drill Site 4-6, the mud ouside the casing became completely frozen. Experimentally measured freezeback times agreed well with calculated (ref. 3) values.

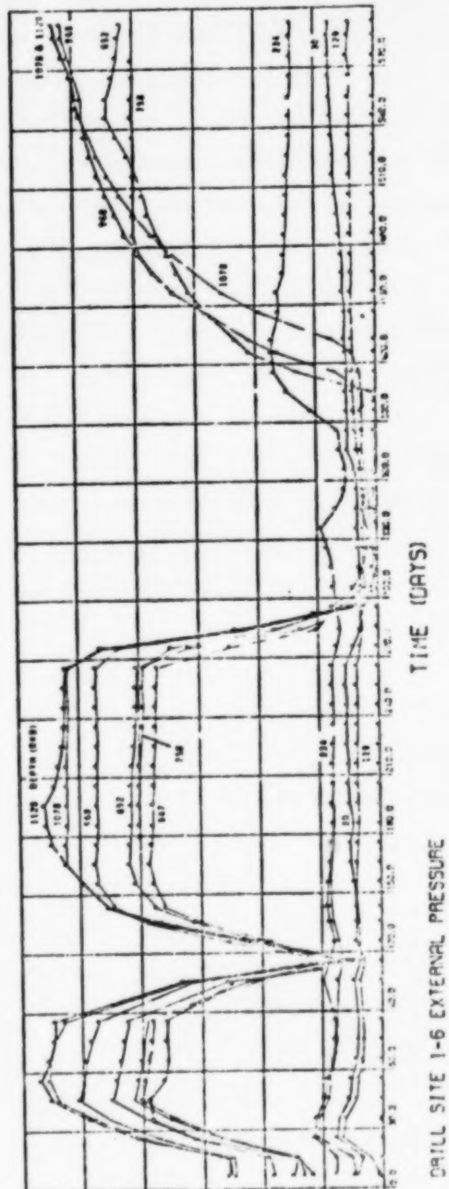
Pressures external to the 13-3/8-inch casing were recorded each 6 hours during both the thaw and refreezing parts of each cycle. The pressure history for the two wells is shown in figure 1. Initially, the transducers indicated a pressure gradient equal to the hydrostatic gradient of the fluid outside the 13-3/8-inch casing. However, during the heating cycles the pressure measurements indicated a drop in the fluid level in the casing-borehole annulus. The drop in fluid level was confirmed by refilling the annulus. The nonlinear behavior of the pressures with depth later during the heating cycles indicated barriers to vertical communication outside the casing of both wells. This is more pronounced during the second heating cycle due to additional sloughing that took place during the first cycle. The nonlinear pressure variation with depth is illustrated on figure 1 where during the second heat cycle on Drill Site 4-6, all of the deeper transducers indicated pressures of less than 200 psi with the exception of the transducer at 571 feet. Similar conditions are shown during the second heat cycle on Drill Site 1-6 where the deeper transducer pressures dropped below 200 psi. The shallower transducer pressures in both wells remained at or near a fluid gradient due to the annulus being filled periodically with water at the surface during the heating cycles.

Immediately following the discontinuation of each heat cycle, pressures began to increase. The pressures in well Drill Site 4-6 increased at each transducer level as the temperature dropped to the freezing level and continued to increase until the temperature fell below the freezing point at that particular transducer level. The independence of each transducer in well Drill Site 4-6 is illustrated on figure 1 where the maximum pressure at each transducer depth occurred as the temperature dropped below freezing regardless of the pressure level of the adjacent transducers. The water-base mud left in the annulus froze across each of the transducers, preventing a vertical transfer of the pressure in the annulus.

The pressure behavior differed in well Drill Site 1-6 because of the presence of the oil-base mud left in the annulus during the completion of this well. The oil-base mud, which does not freeze or



DRILL SITE 4-6 EXTERNAL PRESSURE



DRILL SITE 1-6 EXTERNAL PRESSURE

Figure 1. External pressures measured at D.S. 4-6 and D.S. 1-6 during thawing and refreezing.

solidify, allows the vertical transfer of pressure in the annulus. This explains groups of transducers reaching a maximum pressure at the same time, independent of the temperature level at each of the transducers. This is illustrated on figure 1 in cycle No. 1 where maximum pressures were reached at transducer depths of 30, 129, and 337 feet, simultaneously. Also, a group of transducers at 547, 652, and 968 feet reached maximum pressures simultaneously. This would indicate vertical barriers in the annulus at 450 feet ± and 1,000 feet ± The same grouping of transducers is also apparent during the second cycle. The location of these two barriers, plus additional minor barriers, was indicated by bonding on a Cement Bond Log run prior to and following the second heating cycle.

In addition to the large-scale field experiments, extensive theoretical (refs. 5,6) and computer studies, and laboratory investigations of permafrost properties have been undertaken to more completely understand the freezeback phenomena. The theoretical understanding begins with a computer simulation of thermal behavior since it is the thawing or refreezing of permafrost that leads to its influence on the well. The mechanical behavior of thawed and frozen soils has been determined experimentally (refs. 7,8). Using the results of the experimental studies and the theoretical equation relating stress and strain, a computer program has been developed (ref. 4) that calculates refreezing pressures. Pressures calculated with the computer program agrees with the field data which are shown on figure 1. Figure 2 shows, for example, the maximum freezeback pressures as a function of depth for the various thaw cycles of the Drill Site 4-6 well. These data indicate that multiple cycles do not strengthen permafrost. Figure 3 shows similar behavior for the Drill Site 1-6 well. Heat loss from this well was lower than for the Drill Site 4-6 well because of the low thermal conductivity of the oil-base fluid outside the 13-3/8-inch casing. Maximum pressures observed for this well were generally lower than for the Drill Site 4-6 well because the thaw radius was smaller and because the oil base fluid outside the casing could not

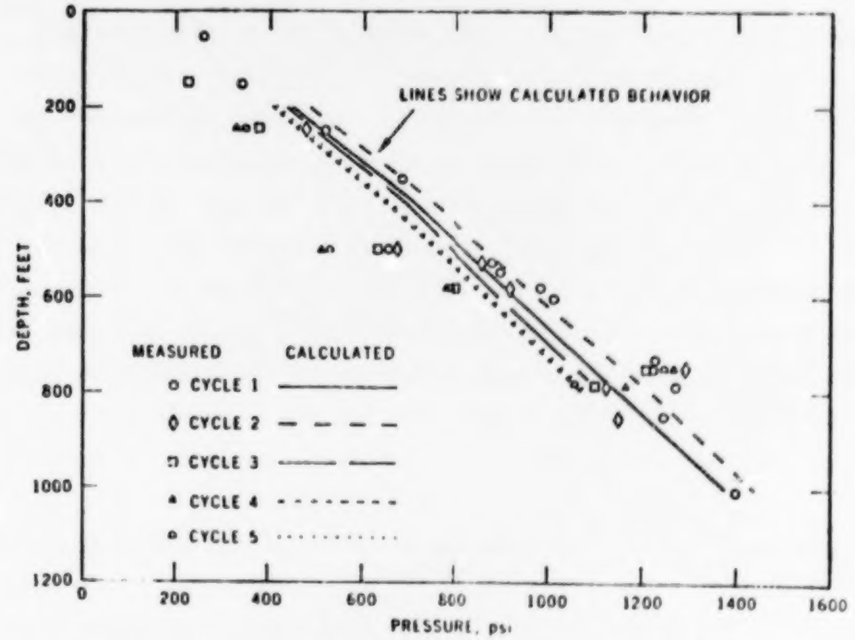


Figure 2. Maximum freezeback pressure Drill Site 4-6.

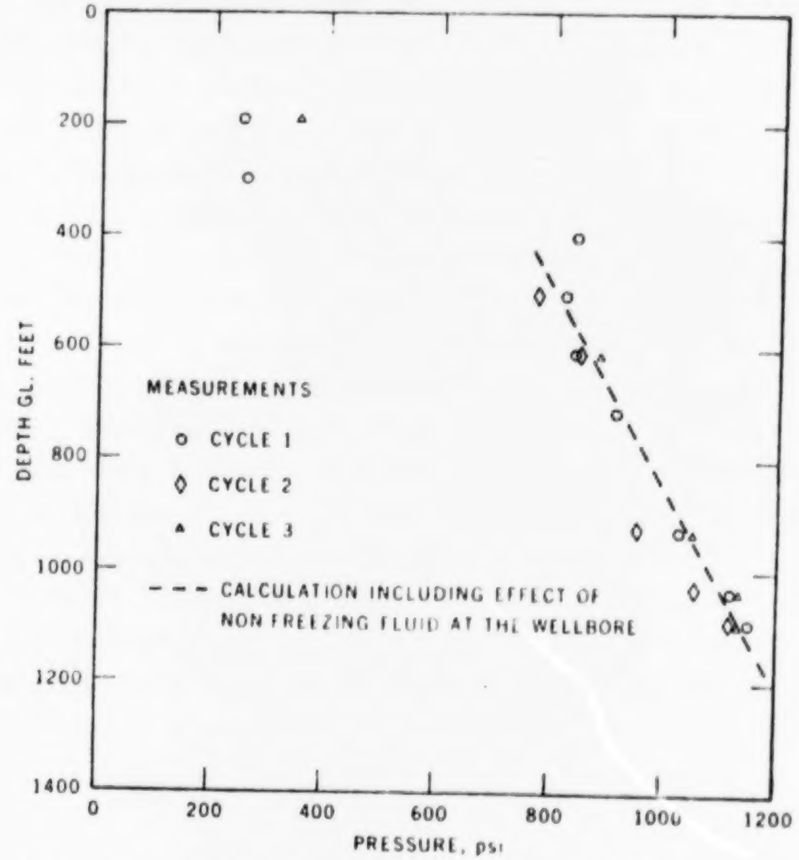


Figure 3. Maximum freezeback pressure Drill Site 1-6.

freeze and create excess volume. The refreezing pressure gradient appeared to be lower in the region above 400 feet where large washouts were logged. Pressure transducers in the interval from 547 to 968 feet reached maximum pressure simultaneously and were related by the hydrostatic gradient of the oil-base fluid surrounding the pressure transducers. Figure 3 also shows calculated behavior including the effect of nonfreezing fluid at the wellbore. This analysis indicates that fluid communication through the annulus of unfrozen oil-base mud causes shallow freezeback pressures to be larger than they otherwise would be, and deeper freezeback pressures are less than they would be if the outer casing annulus were cemented or filled with a freezable liquid.

The previously described computer program has been used to calculate freezeback pressures for field operating conditions. In a typical field case, the degree to which water can flow into the thawed region to maintain saturation, or the degree to which liquid can flow out of the thawed region to relieve pressure, is not known with certainty. In order to calculate a maximum likely pressure, we have assumed that the thawed region will remain saturated during heating and that no fluid can escape from the thawed region during refreezing. The thaw radius depends on the exact well completion and on operating conditions. To illustrate behavior that is expected, we have modeled a well which is completely cemented to the surface and which is insulated with a gelled oil fluid in the 13-3/8-inch by 9-5/8-inch annulus as well as in the 9-5/8-inch by 5-1/2-inch annulus. The well is assumed to be produced at moderately high flow rates for various lengths of time and then shut in to allow complete freezeback to the wellbore. Calculated freezeback pressures versus depth for refreezing after one year of production and for refreezing after 20 years of production are shown on figure 4. Estimated times to refreeze at various depths are also shown. These calculations indicate that somewhat greater pressures are expected for large thaw radii, provided a mechanism is available to resaturate the thawed zone. On the other hand, extremely

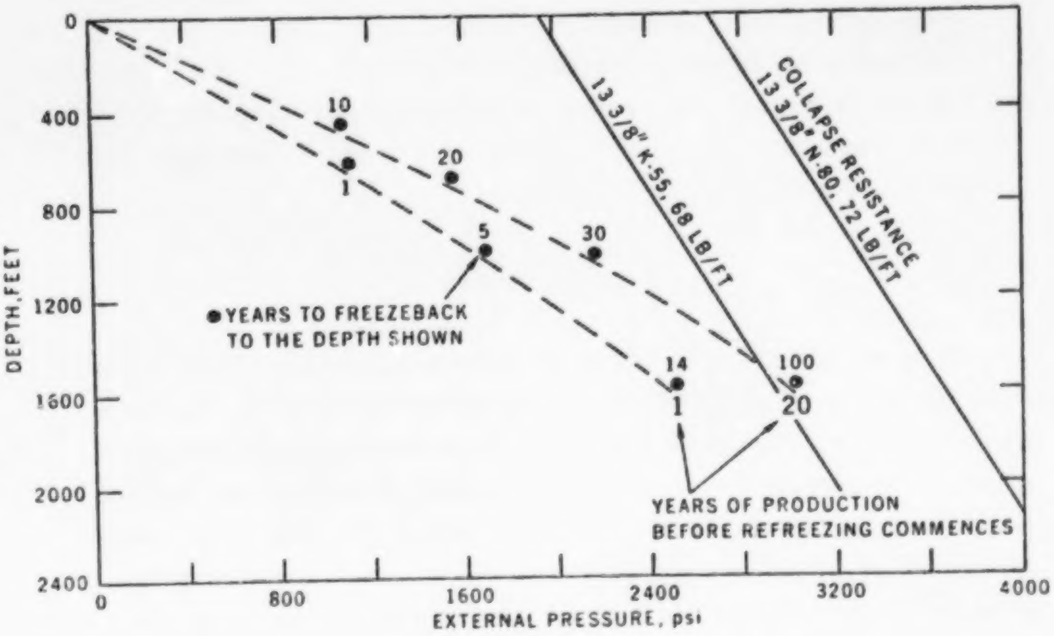


Figure 4. Casing strength (casing full of 9.6 PPG fluid) and estimated maximum freezeback pressures

long periods of time would be required to refreeze and thus generate the pressures. Figure 4 also shows the collapse pressure of two weights of casing when filled with 9.6 ppg fluid and assuming no additional strength resulting from the surrounding cement.

A parameter study has helped to identify important variables. In the course of this study, freezeback pressures were compared with that calculated for the following case:

(Porosity) (Ice Saturation) = 35%
Initial thaw radius = 5.3 feet
Depth = 1,000 feet
Earth stress = 645 psi
Permafrost equilibrium temperature = 22.3°F
Freezing temperature = 31.0°F

Final freezeback radius = 0.557 feet (13-3/8-inch casing)

Freezeback time = 200 days

The effect of parameter variation is shown on table 2. The greatest changes in pressure occur when changing the maximum thaw radius and the final freezeback radius. Of course, it is also clear that depth is a significant variable.

INTERNAL FREEZING

Consider now the possibility of having water-base fluids in portions of the cased wellbore within the permafrost region. As permafrost refreezes, the water-base fluid also refreezes and expands in volume. Pressure will rise until the excess volume can be accommodated by fluid compressibility or expansion of the pipe. If large volumes of fluid are frozen, the pressure may increase to a value which will cause casing damage. Many solutions to this potential problem have been proposed such as (refs. 9-13) displacing the freezable liquid with nonfreezeable fluids or cement, removing undesirable fluids by swabbing and gravity drainage of the annulus, or by drilling the well with an oil-base drilling mud. One of the most attractive solutions is to displace the freezable liquid with an oil-base fluid which gels when it is heated by produced fluids in the wellbore. Such gelled oils can be formulated to have low thermal conductivities and also retard radiant heat transfer. Since gelling suppresses convective heat transfer, the gelled fluid serves as a thermal insulator.

Displacement of water-base mud with large excess volumes of gelled oil has been described previously (ref. 9). More recently, a modified displacement process has been used which improves the efficiency of the displacement operation and reduces cost.

Figure 5 shows a typical well completion. As explained in the previous section of the paper, when casing of adequate strength is employed, it will be satisfactory from a freezeback point of view to cement annuli external to the 20-inch and 13-3/8-inch casings. The

Table 2. Parameter variation results

Initial thaw radius, ft	Pressure, psi	Computed freezeback pressure / Computed freezeback pressure for base case
1	1218	0.77
2	1388	0.88
5	1567	0.99
5.3	1582	1.00
10	1672	1.05
20	1678	1.06

Final freeze radius, ft	Pressure, psi	Computed freezeback pressure / Computed freezeback pressure for base case
0.557	1582	1.00
0.75	1517	0.96
1.0	1467	0.93
1.5	1378	0.87
2.0	1312	0.83

(Porosity) (Ice Saturation), %	Pressure, psi	Computed freezeback pressure / Computed freezeback pressure for base case
1.10	1418	0.90
0.20	1508	0.95
0.30	1562	0.99
0.35	1582	1.00
0.40	1602	1.01

Freezeback time, days	Pressure, psi	Computed freezeback pressure / Computed freezeback pressure for base case
50	1587	1.00
100	1584	1.00
200	1582	1.00
300	1581	1.00
500	1580	1.00

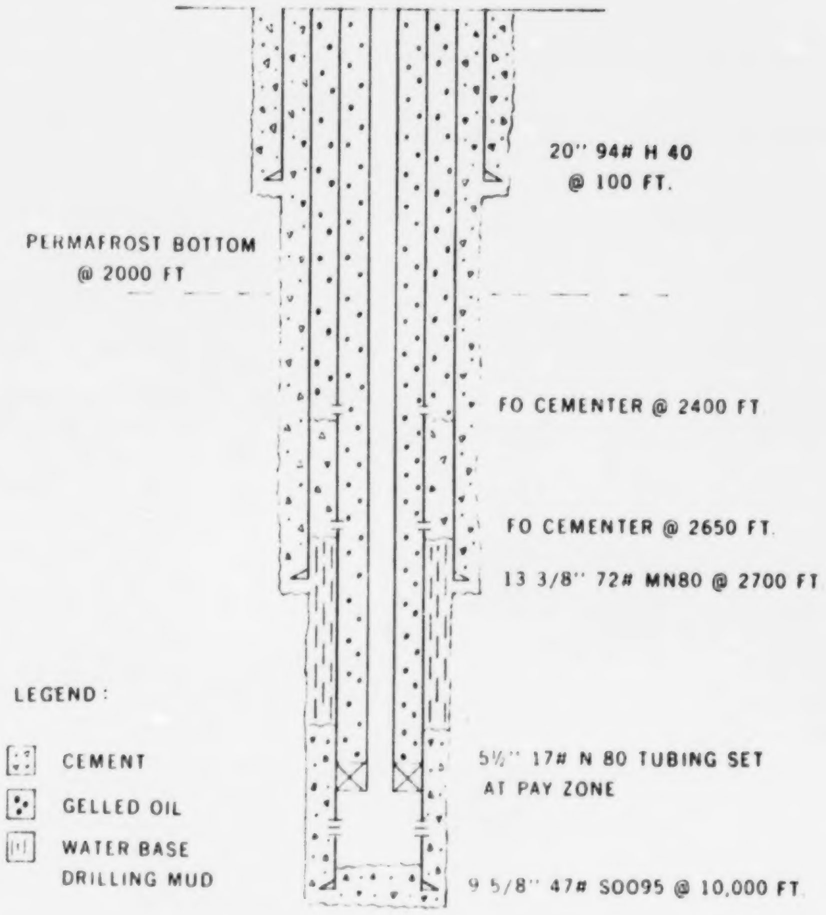

20" 94# H 40
@ 100 FT.
PERMAFROST BOTTOM
@ 2000 FT
FO CEMENTER @ 2400 FT
FO CEMENTER @ 2650 FT.
13 3/8" 72# MN80 @ 2700 FT
LEGEND:
CEMENT
GELLED OIL
WATER BASE
DRILLING MUD
5½" 17# N 80 TUBING SET
AT PAY ZONE
9 5/8" 47# SOO95 @ 10,000 FT.

Figure 5. Typical arctic completion.

annulus between 9-5/8-inch casing and 13-3/8-inch casing can be displaced through a stage cementing tool located well below the bottom of the permafrost. The water-base drilling mud which is being displaced will generally have a modest plastic viscosity and gel strength. Oil-base displacing fluids have been formulated which will irreversibly develop gel strengths sufficiently high to prevent convection as they are heated by produced fluids in the wellbore. During initial placement, the fluid is quite pumpable, yet it exhibits a relatively high plastic viscosity and gel strength even when injected at a low temperature. Because of the high viscosities and gel strengths of these two fluids, a direct displacement is usually in laminar flow. High displacement efficiency of the drilling mud requires that a considerable excess volume of gelled oil be injected.

The more recently developed process includes an intermediate wash step using fresh water. Because of the lower viscosity, high pump rates will produce turbulent flow in the displacing water. If water is pumped down the drill pipe so as to enter the casing annulus and displace mud upwards, the viscosity ratio and gravity ratio in the annulus are unfavorable. Nevertheless, displacements can be relatively efficient. Turbulent eddies erode bypassed mud, transfer it laterally into the moving fluid stream, and thus lead to good displacement efficiencies which are characteristics of turbulent conditions. Displacement behavior during this step has been studied in small laboratory models (approximately 5 and 10 feet long) in an intermediate depth well (900 feet) and in full-scale displacements at Prudhoe Bay. Figure 6 illustrates, for example, the types of displacement behavior observed. The data indicate that no more than two system (drill pipe plus annulus) volumes should be required to achieve good displacement of the water-base drilling mud.

Following the water wash step, gelled oil is injected down the drill pipe to displace the water. If desired, a wiper plug between oil and water can be used. As the weighted gel enters the annulus, both gravity and viscous forces will be favorable. Further, the displaced fluid will have a low viscosity and no gel strength. Studies in laboratory models and in actual field displacements indicate highly efficient displacements. Figure 7 shows a comparison of typical results. Again, less than two system volumes appears to be adequate to achieve a near perfect displacement.

Use of a device to directly indicate water contamination of the gel in the effluent stream has proven to be very helpful. A commer-

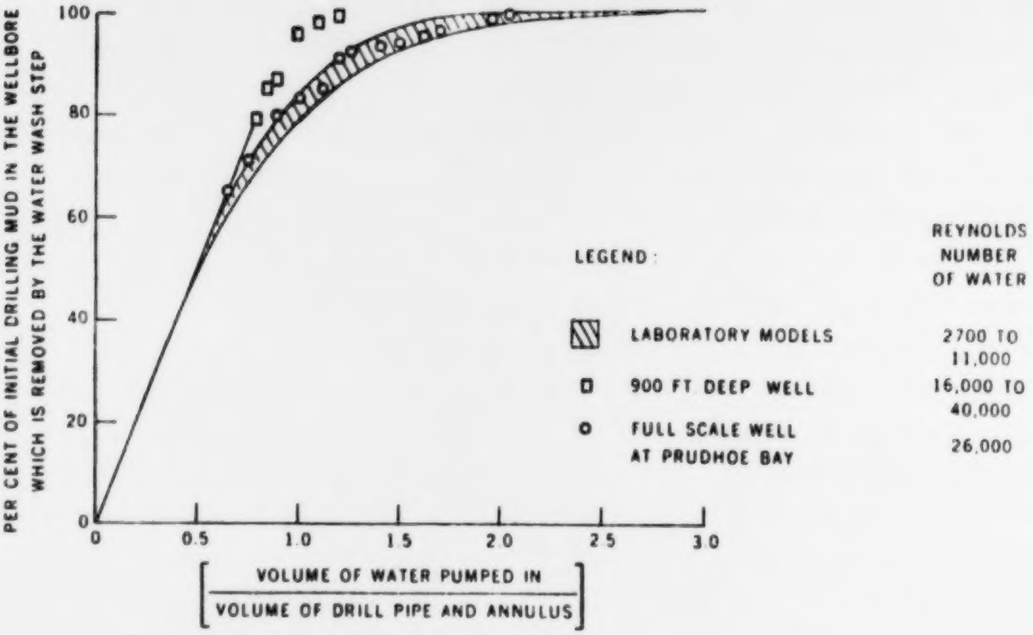


Figure 6. Displacement efficiency during the water wash step.

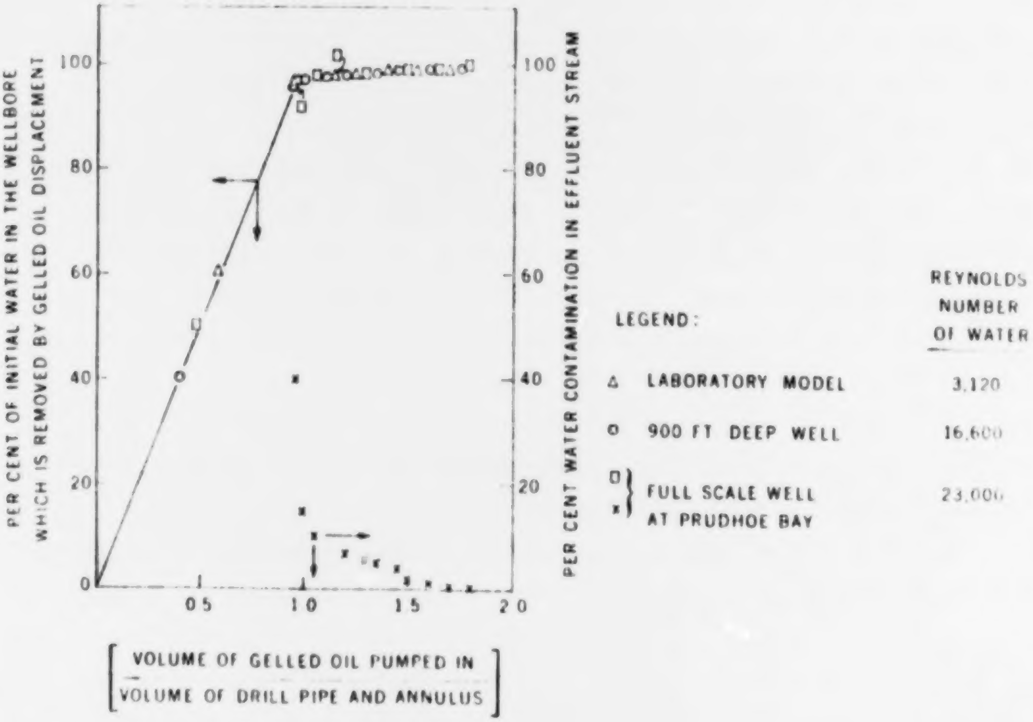


Figure 7. Displacement efficiency for water being displaced by gelled oil.

cially available "Net Oil Analyzer" has been successfully used at Prudhoe Bay. It consists of a Teflon-coated metal probe located centrally in a length of Teflon-coated pipe, both of which are wired to an electronic oscillator circuit mounted integrally with the unit. The electrical capacitance of the device depends on the composition of the fluid in the pipe. This causes the oscillator to generate outputs of various frequencies. By calibrating output frequency against samples of gelled oil containing known water contamination, the probe can be used to monitor the effluent during gel placement. The reading is instantaneous and can be taken as often as desired. For field displacements, a comparison of probe readings with retort analysis of effluent samples has shown excellent agreement.

CONCLUSIONS

1. Field experiments have shown that within the earth, there are mechanisms available to maintain positive pore pressures in thawing regions around a wellbore.
2. Upon freezing, pressures will rise until excess fluid can be dissipated, or until the frozen soil can be pushed back at a rate nearly equal to the rate at which excess volume is being created by the refreezing process.
3. Pressures calculated with a mathematical model which is based on thermal and mechanical behavior of Prudhoe Bay permafrost are in good agreement with values measured in a large-scale field test.
4. Pressures estimated for normal operating conditions are in a range that can be tolerated if the proper casing is selected.
5. In the completion of a typical Arctic oil or gas well, water-base fluids which are inside casing opposite the permafrost section must be removed in order to prevent casing damage resulting from freezing of the fluid.
6. If freezable fluids are displaced by gelled oil, freezing problems will be eliminated while at the same time the gelled oil serves as a thermal insulator.

7. An improved displacement process consists of an intermediate water wash step to displace drilling mud before injection of gelled oil.

8. Two system volumes of water are sufficient to remove virtually all the water-base drilling mud from the system.

9. Displacement of water with weighted gelled oil is highly efficient, and less than two system volumes has given near perfect displacements.

10. Use of readily available electronic instruments permits continuous monitoring of the gelled oil effluent stream.

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DISCUSSION

MR. GENE J. MIROLLI SPE-AIME (Hercules, Inc., Beaumont, Texas): Have you investigated the use of insulated casing? If so, does it show any improvement in projecting permafrost?

MR. KNOWLES: Yes. This has been what we would call a contingency study. Anytime you embark on a problem of this magnitude where you are doing original work, you obviously do not put all of your eggs in one basket.

And, yes, we have looked at several different types of dual wall tubing and casing, and different insulation materials.

The need for insulation all relates to the interrelationship of what the effect of the oil well is on the permafrost, and what the effect of the permafrost is on the oil well. Understanding this, one soon determines what degree of insulation is required. It is not the black and white problem of whether you are going to insulate or you are not going to insulate. The answer lies somewhere in the gray area. You only need to insulate to a given degree.

All our studies to date, and we are talking about the combination of about 3 years of work, now indicate that a limited thaw technique, using oil-base casing pack, has a very acceptable safety margin.

MR. RICHARD S. SCALAN (University of Texas, Marine Sciences Institute, Port Aransas, Texas): I wonder if you could give the uninitiated an idea of what permafrost is like. Is it something like jelly? Would you sink up to your knees in it?

MR. KNOWLES: That is an excellent question.

The Arctic Slope that we are working on--specifically, the area west of the Canadian border and east of the Bering Straits, the North Slope of the Brooks Range--has a very interesting geologic background. I make no pretense of making these comments as an expert, but just on what I have garnered from my studies with geologists.

In the formations at about 1,200 to 1,000 feet, we find evidence of ferns, fossils, and micro fauna that one would find in a subtropic climate. The formations that are now in the range of 900 to 600 feet--when they were at the surface and being deposited--the climate was, in general, an Alpine one, much as we have in Anchorage or in the high Rockies in Idaho or Colorado.

A very lengthy study has been made to determine how much of the formation was laid down in frozen conditions. The results of this study indicate that the sediments above 200 feet are the only portions of the formation that have been laid down under Arctic conditions.

Unfortunately, when you speak of permafrost, the picture that immediately jumps to mind is the classic muskeg. One picture is in the wintertime of a frozen swamp with a Caterpillar tractor walking across it, and then the next picture is in the summertime when you could not wade across the swamp. That is characteristic of the upper perhaps 30 to 50 feet in the area in which we are dealing.

Below 200 feet, certainly you are talking about formations that were laid down under thawed conditions, with normally compacted grain-to-grain contact.

And so the answer to your question of what is the permafrost to a drilling engineer is: permafrost is like any other frozen gravel bed. It is frozen; it has ice between the grains. It has none of what we refer to as excess ice. The load carrying member is the grain itself.

The classic muskeg is in the upper 50 feet, perhaps in the upper 30 feet, where you have a lot of excess ice. You have the polygons, obviously as the result of the ice wedges. We have a great deal of information on that, but that gets over into the civil engineering problem of structure support. In the oil well problem, we are looking at the overall 2,000 feet of permafrost, and we are talking about grain-to-grain contact through that section.

DRILLING FLUID PRINCIPLES AND OPERATIONS

Jay P. Simpson*

Abstract

The purpose of this discussion is to tell what drilling fluids are and to explain why drilling fluids must be used. Emphasis is given to the functions of a drilling fluid--what the drilling fluid must do. This, in turn, is related to the physical and chemical properties of the drilling fluids that are tested and controlled, so that drilling operations can be conducted safely and effectively.

Since a great diversity of drilling conditions are encountered, many types of drilling fluids must be used. Some of the most widely used types of drilling fluids are described, with attention to why these systems are selected. Although a variety of materials are used to prepare and maintain each type of drilling fluid, the additives can be considered in certain general classes. These classes of materials are discussed in relation to the physical or chemical properties to be controlled. Consideration is given to the relative quantities of materials used in a typical drilling fluid.

Some of you out there may be asking yourselves these questions: "What is a drilling fluid? Why does anyone have to use one? Why does it need to be so complicated? Why do we use so many different materials?"

Perhaps one of the reasons that it is difficult to talk about drilling fluids is that we cannot really see what is going on down where the drilling fluid is doing its work. However, I will try to describe the procedure.

The drilling fluid will start in the suction bit. A mud pump will move the drilling fluid up into the drill string. The drilling fluid really starts its work as it goes out of the eyes of the bit, because what it must do is move the cuttings away from the bit and transport them on up the hole.

I think you can see that if it does not do that job, the drilling operation is not going to last very long.

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Let us follow the course of the drilling fluid, as it brings the cuttings back up the annulus between the drill string and the wellbore. At the surface, the drilling fluid flows out the flow line and usually is passed over a shale shaker--a vibrating screen where the cuttings are separated and dumped into a shale pit. The drilling fluid falls through the screen into a settling pit and then moves on over into the suction pit to start the cycle again.

The circulation system can vary a great deal. A typical arrangement on a big rig might include three tanks for the surface system. For an air drilling operation, instead of the mud pump there would be air compressors that would pump air down the drill string and back out the flow line.

Now, let us get to the matter of why we have to use a drilling fluid. The primary functions of a drilling fluid are listed in table 1. Serving any one of these functions might be fairly simple; but when we put them altogether, it does get quite complex. We have already talked about transporting drill cuttings to the surface, and many different fluids will do this. The simplest perhaps would be just circulating air.

The second function listed has to do with control of formation pore pressures. In many ways this is perhaps the single most important function of the drilling fluid.

Hydrostatic pressure is provided by the drilling fluid. This, coupled with the pressure drop at the drilling fluid travelling up the annulus, constitutes an equivalent circulating density that can balance a pore pressure.

Table 1

PRIMARY FUNCTIONS OF DRILLING FLUIDS

- TRANSPORT DRILL CUTTINGS TO THE SURFACE
- CONTROL FORMATION PRESSURES
- MAINTAIN BOREHOLE STABILITY
- PROTECT PRODUCTIVE FORMATIONS
- PROTECT AGAINST CORROSION
- COOL AND LUBRICATE THE BIT AND DRILL STRING

But it is going to balance only one pore pressure. Down hole we will have many pore pressures. The exposed formations will not all be at the same pressure.

Perhaps the most common practice would be to adjust the drilling fluid density to balance the highest pressure encountered in a permeable formation. If you do not do that, the formation fluids will move into the wellbore, move the drilling fluid out, and you will have an uncontrolled well on your hands.

Selecting the density of the drilling fluid, however, may not be that simple. The next function of a drilling fluid listed in table 1 is that of maintaining borehole stability. If we are just balancing the pore pressure of a permeable sand, and we have a shale that is under higher pressure--and this is a quite common situation--we do not have sufficient pressure to completely support the shale. Therefore, there will be a force tending to push that shale into the wellbore, causing spalling or sloughing and resulting in borehole enlargement.

The mud chemistry can often be modified to tolerate a degree of pressure underbalance without too much hole enlargement. Many shales, however, may be so unstable that the drilling fluid density will have to be increased to balance the pore pressure in the shale creating a considerable overbalance opposite the lower-pressure sand. The differential pressure will then push the filtrate out of the drilling mud and into the formation.

The weight material and drill solids will be left on the wellbore as wall cake, and the hole will fill up with wall cake unless we do something about it. The filtration properties of the drilling fluid must then be controlled. This ties in with the function of protecting productive formations.

If permeable sand is the zone from which we hope to produce oil or gas, and if we allow a great deal of filtrate to enter that formation (or even worse, if we allow whole mud into that formation), we can pretty effectively block and damage the formation. In many productive zones, there will be clay materials that are sensitive to filtrate from just an ordinary water-base mud, so you could have some serious damage from even small volumes of filtrate. To combat this, we do certain things to the chemistry of the drilling fluid to limit the hydration, swelling, and movement of clay particles in a dirty sand.

Another function of drilling fluid that we cannot ignore is protection against corrosion. In our drilling operations, the drilling fluids do incorporate air. Oxygen then is available to cause an oxidation type of corrosion. We also encounter acidic gases such as carbon dioxide and hydrogen sulfide. It is the drilling fluid that gives us the capability of creating a situation where the tubular goods (the drill pipe and the casing), can be protected. Or we can at least use the drilling fluid as a means of delivering corrosion inhibitors to protect the pipe and the casing.

Finally, the drilling fluid must cool and lubricate the bit and drill string. Air might do this under certain conditions; on the other hand, some operations may require very special attention to this matter of lubrication. For example, in drilling from an offshore platform, many wells (perhaps 20 or more) might be drilled out directionally and then turned to the zones to be produced. These high angle holes put quite a burden on the drilling fluid to provide sufficient lubricity. Special additives are used to provide the lubricity needed.

Let us consider some of the types of drilling fluids that are used. These are listed in table 2. If an operator had his choice, he would probably pick the first type - air or gas - because the gaseous fluid would provide the fastest drilling rate and least chance of formation damage. Unfortunately, there are not very many situations where merely air or gas would be sufficient. The second choice would likely be clear water or brine. Again, there are not many cases where this could be used. This brings us down to the water muds. These are the clay-base muds (usually dispersive

Table 2

TYPES OF DRILLING FLUIDS

- AIR OR GAS (MIST, FOAM)
- CLEAR WATER OR BRINE
- WATER MUDS (CLAY-BASE, POLYMER)
- OIL MUDS

systems) and the polymer muds (usually nondispersive). These are the drilling fluids that are used in most of the drilling operations today.

If none of the above systems will do the job, then the last resort will be to go to an oil mud. This would be mud that has oil as the continuous phase. Any water that is added or incorporated will be thoroughly emulsified as a dispersed liquid phase.

Let us consider some of the conditions in table 3 that would permit air or gas drilling. We said that the drilling fluid provides the hydrostatic control for formation pore pressures that are encountered. If these are low, then air-gas drilling might be conducted. Strong competent formations would also be necessary, because if the formation was weak it still would collapse into the wellbore even though you could handle the small volumes of gas that might come in.

Table 3

CONDITIONS FOR AIR OR GAS DRILLING

- LOW FORMATION PRESSURES
- STRONG, COMPETENT FORMATIONS
- NO HIGHLY PERMEABLE FORMATIONS CONTAINING WATER OR OIL

For clear-water drilling (as shown in table 4) we would need normal or subnormal formation pressure, because we would have nothing there except the hydrostatic pressure of the water itself to control formation pore pressures. In highly permeable formations, there would be loss of the drilling water into the formation, and you would not be able to maintain circulation.

Table 4

CONDITIONS FOR CLEAR-WATER DRILLING

- NORMAL OR SUBNORMAL FORMATION PRESSURES
- NO HIGHLY PERMEABLE FORMATIONS
- NO EXTREMELY WATER-SENSITIVE SHALE FORMATIONS

Water-sensitive shale would give an unstable hole when drilled with a clear-water system.

If any of these conditions exist, we will have the need to use a liquid mud. For example, if we have abnormally high pore pressure, then we will need to have a drilling fluid that can be weighted. Since this calls for suspension of the weighting material, we then get into the area we call mud. If we have highly permeable formations, we need filtration control. And if we have water-sensitive shales, we use those materials that slow down the entry of water into the shale.

Listed in table 5 are conditions that create problems when drilling with a water mud. When any of these conditions get too bad, we go to the oil muds. The oil muds are used often for extremely water-sensitive shale formations and for drilling steep, bedded salt. Another use for oil muds is in drilling abnormal pressure formations containing H_2S. The reason for this is that the abnormally pressured wells require the use of high strength pipe for drilling, and high strength pipe is sensitive to sulfide stress cracking. The oil mud protects the pipe from corrosion and stress cracking.

Table 5

CONDITIONS FAVORABLE FOR DRILLING WITH OIL MUDS

- EXTREMELY WATER-SENSITIVE SHALE FORMATIONS
- DEEP SALT FORMATIONS
- ABNORMALLY PRESSURED FORMATIONS CONTAINING H_2S
- FORMATIONS WITH TEMPERATURES EXCEEDING 400°F
- PRODUCTIVE FORMATIONS SUBJECT TO DAMAGE BY WATER

Most of the water mud additives will degrade at temperatures above 300°F and degrade quickly above 400°F. So the more temperature-stable oil muds are likely to be used in very high temperature wells.

Table 6 relates some of the functions of the drilling fluid to the composition or property that is controlled. For cuttings transport, materials like bentonite are used to increase the viscosity and gel strength. Weighting materials are used to increase the density of the drilling fluid

Table 6

FUNCTION	COMPOSITION OR PROPERTY CONTROLLED
CUTTINGS TRANSPORT	VISCOSITY - GEL STRENGTH
PRESSURE CONTROL	DENSITY
HOLE STABILITY AND FORMATION PROTECTION	FILTRATION - ALKALINITY - SALINITY - WETTING CHARACTERISTICS
CORROSION PROTECTION	ALKALINITY - OXYGEN - SULFIDE - WETTING
LUBRICATION	LUBRICITY

to provide pressure control. The type of material needed is one that has a high specific gravity. We also need a material that is: (1) as chemically inert as possible; (2) as insoluble as we can get; (3) not too hard; and (4) not too soft (because we do not want it to wear down very quickly). Barite, naturally occurring barium sulfate, is used for this purpose.

Hole stability and formation protection can be considered together. For controlling filtration we often use bentonite and polymers and get help from lignite and lignosulfonate. In extreme situations we could change the wetting characteristics by going from a water system to an oil-mud system. For corrosion protection, we generally keep the drilling fluid on the alkaline side. For extreme conditions, we might go all the way to an electrically nonconductive oil mud environment. For lubrication, we pay attention to such things as wear characteristics, coefficient of friction, extreme pressure lubricity, and differential pressure sticking. We then use materials that will help in combating these problems that are associated with drilling deep, high-angle holes.

I think you might be interested in where some of the mud materials come from. Most of the good bentonite comes from surface deposits in the State of Wyoming. The crude ore is brought in, stockpiled, blended, and weathered. It is then dried, ground, sacked, and delivered to the oil field. The deposits of the oil-field grade lignite are located mainly in North Dakota. Lignite is one stage in the change of humus material to coal. We might think of it as a naturally occurring humic acid. Lignite, like bentonite, can be mined, dried, ground, sacked, and made ready to go.

Barite is the material that we use in such tremendous quantities and which is found all around the world. Barite mining is a very simple operation in Missouri. Some of the deposits about a generation ago actually wer worked by hand. The Missouri operation contrasts with the processing of th massive barite deposits at Magnet Cove, Arkansas, where the barite is mined and trucked to a plant. There it is upgraded by a rather sophisticated flotation process to remove the low specific gravity material and get the material we need for oil field operations, which is 4.2 specific gravity, or better than four times the density of water. At various sites around th world, the barite ore will be brought to a processing plant where it will b crushed, dried, and ground. Some of it will be sacked, but some if it will be kept in bulk form so that it can be handled pneumatically and delivered to the rig to bulk tanks.

Not all of the drilling fluid materials are mined products. A lot of them are manufactured in chemical plants and are either sacked or drummed for delivery to the rig for use.

Let us take a look now at what are some of the quantities of materials used in a drilling fluid.

An air or gas drilling fluid, as you might expect, is a very simple system. Typical components are listed in table 7. In this kind of an operation, you can imagine that we do have to pay attention to corrosion, and so there will be some small amount of corrosion inhibitor used. Also some foamers will ordinarily be used to cope with water encountered while drilling. The foamer is injected into the air stream and pumped down the

Table 7

AIR OR GAS DRILLING

COMPONENT	CONCENTRATION, lb/hr
FOAMER (SOAP, DETERGENT)	1 TO 10
CORROSION INHIBITORS	1 TO 5
BENTONITE	50 TO 100
POLYMER (CMC, POLYACRYLATE)	1 TO 5

hole where it encounters water that comes into the well. The water comes out of the well in a kind of mist along with the cuttings. Not very much material is used, maybe 1 to 10 pounds of foamer per hour of drilling operation.

In the more difficult situations, a little bit of water will cause the wellbore to slough some. This means bigger particles to bring out, and this can be handled better with what you might call a stiff foam. In that case a liquid mud would be mixed on the surface--maybe bentonite and a high molecular weight polymer--and then injected into the air stream. When that material goes down the hole, the bigger pieces can be brought to the surface and the air drilling can continue a little longer.

In clear water drilling, the big problem is trying to keep that water clear. I think you can imagine that water circulated while drilling tends to get dirty. To help prevent this, you might use a flocculant such as guar or a polymer such as a polyacrylamide. As shown in table 8, the amount used might be as low as 0.05 lb/bbl.

Table 8

CLEAR WATER DRILLING

COMPONENT	CONCENTRATION, lb/bbl
FLOCCULANTS (GUAR, POLYACRYLAMIDE)	0.05 TO 0.5
FIBROUS MATERIAL (PAPER, ASBESTOS)	2 TO 5 (BATCH)
CORROSION INHIBITORS	--

Occasionally the practice will be to pump down a batch of water that contains fibrous materials (perhaps shredded paper or asbestos) to sweep larger particles out of the hole. Sometimes corrosion inhibitors are used in this type of drilling.

For the water-base muds, we could have a hundred examples. Probably the most widely used system is a fresh water mud treated with lignite and lignosulfonate, such as shown in table 9. The amount of barite required will depend upon the formation pressure encountered and would be on the order of 500 pounds of barite for one barrel of drilling fluid having a density of 18 pounds per gallon.

Table 9

CLAY-BASE MUD

COMPONENT	CONCENTRATION, lb/bbl
WATER	200 TO 340
BENTONITE	15 TO 30
LIGNITE	1 TO 6
LIGNOSULFONATE	2 TO 10
SODIUM HYDROXIDE	0.5 TO 1.5
BARITE	0 TO 500

It might be worth pointing out that the density of the drilling fluid ordinarily would not have to exceed the density of the overburden, about 19 pounds per gallon. Therefore 18-pound mud is about as high as you would have to go.

As shown in table 10, a polymer mud would be very much like the dispersive type clay-base mud. The salt concentration would be about 100 lb/bbl when sodium chloride is used. If potassium chloride is used, you might need only 10 to 20 lb/bbl. The alkaline material (hydroxide) is added for pH control, because drilling with acidic mud tends to cause corrosion problems

Table 10

POLYMER MUD

COMPONENT	CONCENTRATION, lb/bbl
WATER	300 TO 345
BENTONITE	0 TO 10
SALT (NaCl, KCl)	10 TO 100
SODIUM OR POTASSIUM HYDROXIDE	0.1 TO 0.3
POLYMER (STARCH, POLYACRYLAMIDE)	0.5 TO 5
BACTERICIDE (PARAFORMALDEHYDE)	0.1 TO 0.5
BARITE	0 TO 300

As indicated in table 11, oil muds are customarily prepared from diesel oil using some type of surfactant to emulsify water. The filtrate reducer and gellant can be oil-dispersible versions of the lignite and clay used in water-base muds, while the barite is the same as that used in the aqueous systems.

Table 11

OIL MUD

COMPONENT	CONCENTRATION, lb/bbl
DIESEL OIL	150 TO 230
WATER	35 TO 50
CALCIUM CHLORIDE	15 TO 25
EMULSIFIER (SOAP, POLYAMIDE)	5 TO 20
FILTRATE REDUCER (AMINE LIGNITE)	0 TO 10
GELLANT (AMINE CLAY)	2 TO 4
BARITE	0 TO 500

The handling of oil muds often differs from that of water-base systems. With water-base muds, the additives are usually delivered to the drill site in bags or drums and then mixed into a mud system using the rig equipment. In areas where a lot of oil mud is used, we quite often will handle it as a liquid mud.

The mud would be mixed in tanks at a liquid mud plant. It would then be delivered to a land location by truck, to inland water jobs by barge, or taken to an offshore location by a delivery vessel. After use at the rig, the oil mud can be brought back to the liquid mud plant, reconditioned, and stored for future use.

DISCUSSION

MR. HARRY L. HARRISON (A.C. Drilling Specialties, Odessa, Texas): On your polymer fluids, I did not hear you mention cellulose materials. Have you had any experience with those, or would you care to comment?

MR. SIMPSON: Yes. Many different polymers are used. I would just select one as an example--carboxymethylcellulose--that is used along with many others.

WELL COMPLETION--TECHNIQUES AND METHODS

Frank H. Braunlich*

Ladies and gentlemen, we have another broad topic to cover--a topic that I have termed "Well Completion." (Figure 1 shown.)

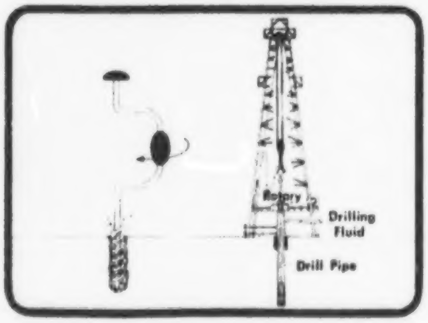
Rotary
Drilling Fluid
Drill Pipe

Figure 1.

We have heard this morning about the techniques and principles of drilling a well. Now we must complete it and prepare it for production. Several operations are required to do this. These well completion operations bascially involve cementing, perforating, and stimulation of the producing formation. (Figure 2 shown.)

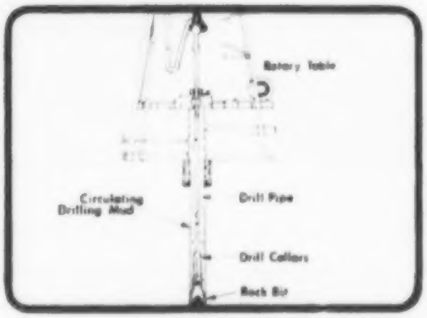
Rotary Table
Circulating Drilling Mud
Drill Pipe
Drill Collars
Rock Bit

Figure 2.

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After the hole has been drilled to the desired depth, it is necessary to run some steel pipe into the hole in order to protect it from contamination and provide communication between the surface and the formation below. (Figure 3 shown.)

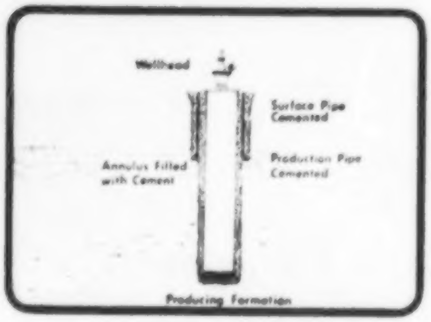

Wellhead
Surface Pipe Cemented
Annulus Filled with Cement
Production Pipe Cemented
Producing Formation

Figure 3.

Cement is used to secure this pipe in the hole. Cement also protects and isolates the various rock formations up and down the hole. In figure 3 we see two strings of casing. The surface string is cemented to its total depth from the surface and a production string is cemented from its total depth through the surface string. (Figure 4 shown.)

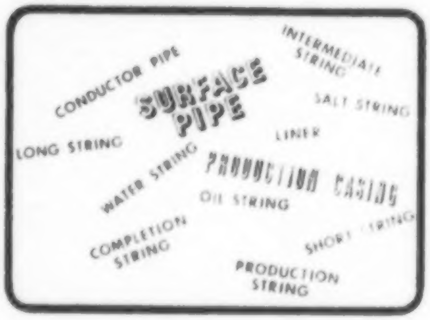

CONDUCTOR PIPE
SURFACE PIPE
INTERMEDIATE STRING
SALT STRING
LONG STRING
LINER
WATER STRING
PRODUCTION CASING
OIL STRING
COMPLETION STRING
SHORT STRING
PRODUCTION STRING

Figure 4.

All wells require a surface string and a production string. However, some wells, depending on the depth and the problems encountered, will require extra casing strings, as we have heard this morning. These have different names, usually defining the job for which they are required. A conductor pipe starts from the surface; we find a water string, a salt string. These are rather self-defining terms for the various casing strings.

The surface string that we have to put into the well is used to control caving and washing out of poorly consolidated formations near the surface. It provides a working area and contact to the earth for the remaining drilling operations. Another very important function of this surface casing is to prevent the freshwater sands from being contaminated with drilling mud, oil, ash, or saltwater. The surface strings vary from maybe 7 inches up to as high as 20 inches in diameter, and they will be cemented from the surface to the bottom. (Figure 5 shown.)

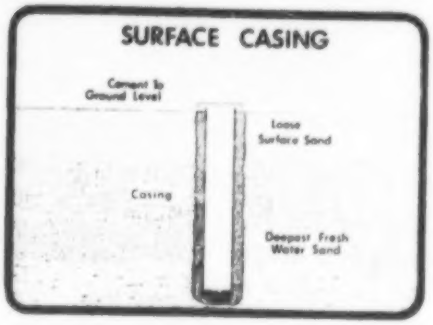


Figure 5.

Regardless of the type of casing run, the same cementing operations are performed to tie these pipes to the formation through which they pass. The length of the surface casing will vary considerably, from a few hundred feet to over a thousand feet, depending both on conditions and on what has been encountered while drilling the well. Some of these problems have been mentioned this morning.

This casing is used to allow access to the producing zone, and it will protect the formation between the producing area and up through the various levels back to the surface. This pipe will usually extend from the ground level through the surface casing and into the zone of expected production. It is not always cemented all the way to the surface, although it may be. It may be exposed to very high pressures, and in some cases to very corrosive fluids as well as high temperature. So it is imperative that the surface casing be extremely well designed. (Figure 6 shown.)

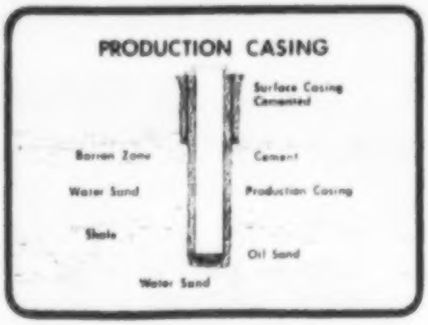

PRODUCTION CASING
Surface Casing Cemented
Barren Zone
Cement
Water Sand
Production Casing
Shale
Oil Sand
Water Sand

Figure 6.

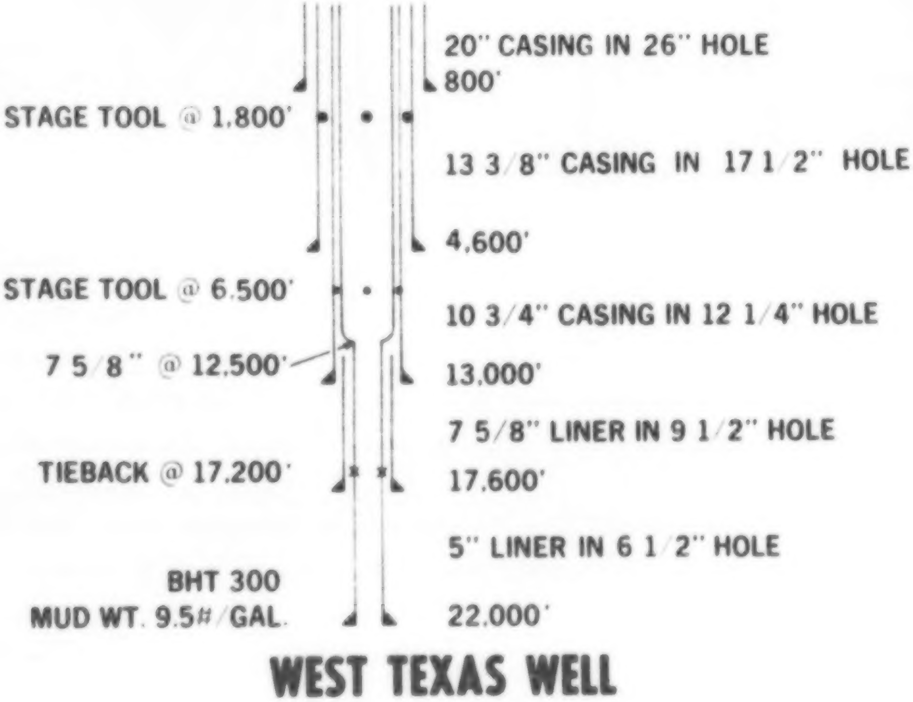

20" CASING IN 26" HOLE
800'
STAGE TOOL @ 1,800'
13 3/8" CASING IN 17 1/2" HOLE
4,600'
STAGE TOOL @ 6,500'
10 3/4" CASING IN 12 1/4" HOLE
7 5/8" @ 12,500'
13,000'
7 5/8" LINER IN 9 1/2" HOLE
TIEBACK @ 17,200'
17,600'
5" LINER IN 6 1/2" HOLE
BHT 300
MUD WT. 9.5#/GAL.
22,000'
WEST TEXAS WELL

Figure 7.

After it is cemented in place, the production casing separates the producing zone from undesirable fluids such as saltwater, and acts as a work shaft to the producing zone. (Figure 7 shown.)

Contrasting the simple well shown in figures 3,5, and 6, with only a surface string and a production string, here is a West Texas well drilled to 22,000 ft. It contains five strings of casing and several special tools. The 800-ft surface string is 20-inch pipe set with cement from 800 feet to the surface. The intermediate string to 4,600 ft was cemented around the bottom 800 ft and by use of the stage tool, from 1,800 ft to the surface.

The next intermediate string was 10-3/4 in. set at 13,000 ft. At this time the formation would not withstand the full hydrostatic head of cement; so cement was placed around the bottom 1,000 ft. and above 6,500 by means of the stage tool.

The next two strings of pipe are called liners. Liners extend from the bottom of the well up into the previous string of pipe. They do not extend all the way back to the surface. The first liner (7-5/8") is set at 17,600 ft and cemented into the 10-3/4-in. casing. The 5-in. liner is cemented from 22,000 ft into the 7-5/8-in. liner. The 5-in. liner contains a tieback tool that allows pipe both to be run to this point and the surface and to be cemented as a production string if the well is determined to be a producer. If it is not a producer, the additional pipe has been saved. (Figure 8 shown.)

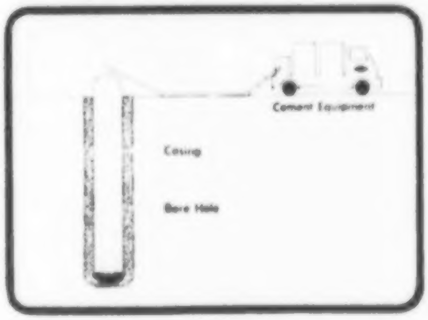


Figure 8.

Surface equipment is rather sophisticated these days. Special trucks and transports have been developed for this. (Figure 9 shown.) We see in figure 9 a transport to haul bulk cement to the well. Most cement is handled in bulk, although it has been and can be handled by sacks. It is taken out in air bottles and transported by compressed air from the air bottles to the cementer.

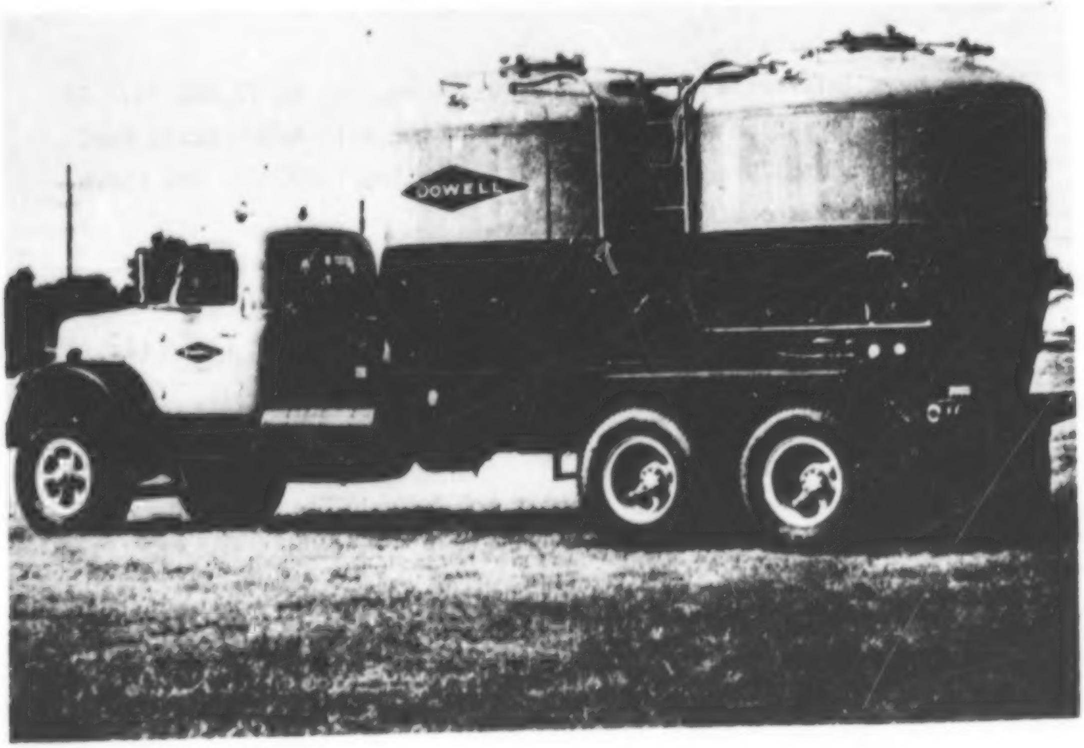


Figure 9.

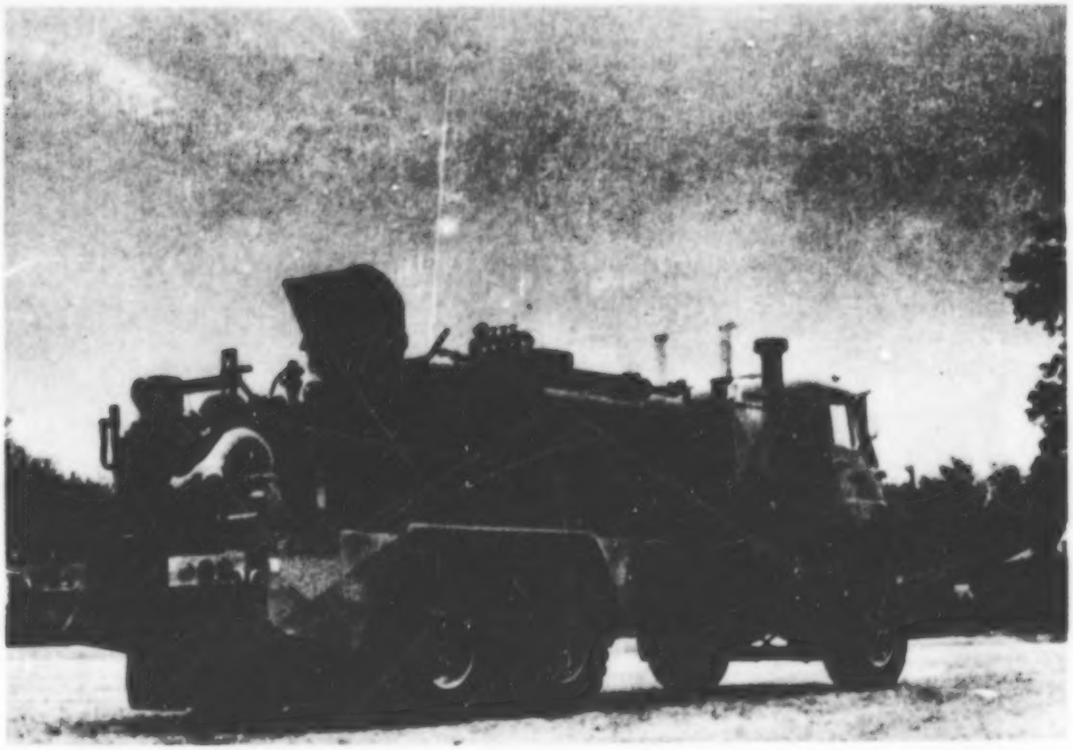


Figure 10.

At the cementer the cement is injected into a mixing device where the water and the dry cement solids are blended together. (Figure 10 shown.) The cementer (fig. 10) consists usually of two pumps and two displacement tanks so that all the pumping operations can be conducted, and so that the amount of cement and following flush fluid that has been pumped can be measured. After coming through this mixing device at the back of the truck, the cement slurry is picked up by a high-pressure pump and pumped into the pipe, thus displacing the drilling mud in the hole. Figure 11 shown.)

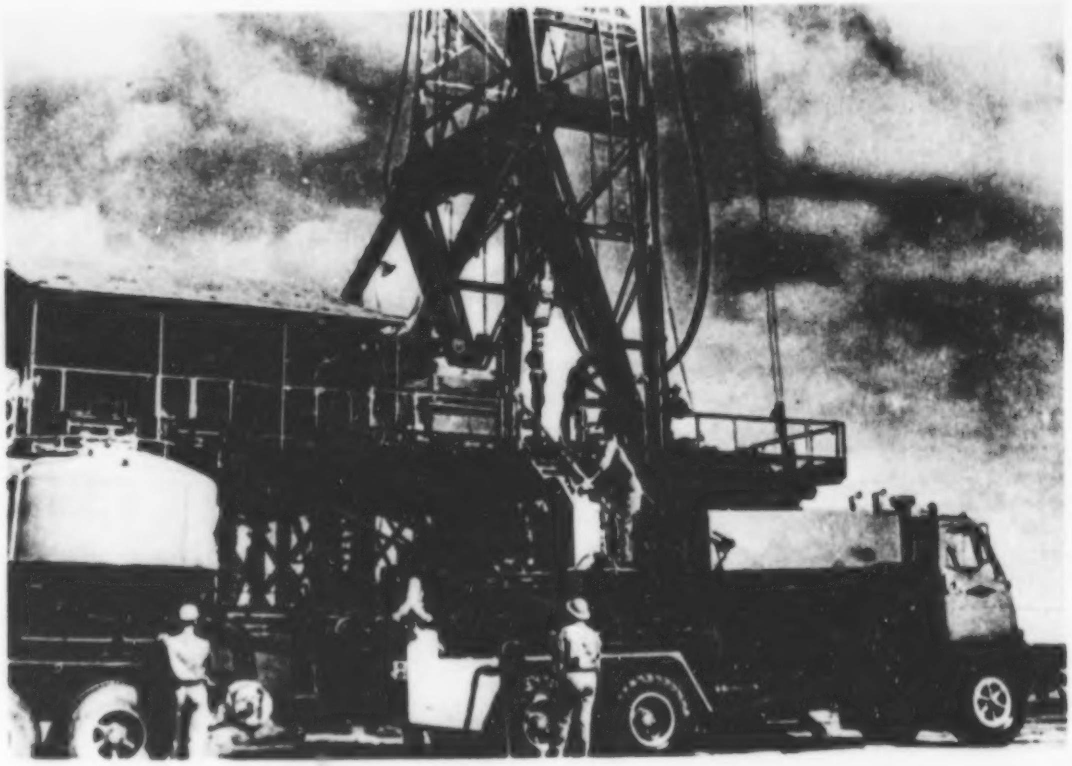


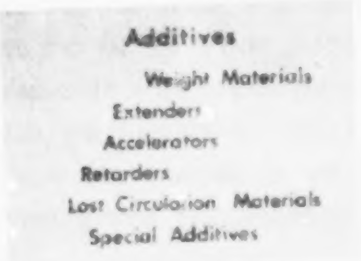
Figure 11.

In figure 11 we see a well site with a cementing operation underway. The dry ingredients, including all of the additives that are needed for cementing, are blended and mixed at a station where everything is stored. They are then brought out in the transport, blown across by air into the blender part of the cementer, and from there picked up and with a high-pressure pump put down through the pipe, much as was shown for the drilling mud. (Figure 12 shown.)

WHY USE CEMENT?

Figure 12.

Why do we use cement? When mixed with water the dry product known as Portland Cement will set into a very hard mass. Before the cement slurry has hardened, it is very easily handled, and we can provide the necessary hydraulic system that we need to do the job. Experience in the oil industry has proven that this readily available material best solves the need to permanently place and seal casings in a well. The most common method of mixing cement is to add water to the dry Portland Cement. This type of cement is called neat cement. However, the neat cement does not answer all the questions and problems that we have, so we have to provide other properties to this cement slurry by using additives. (Figure 13a shown.)



Additives

- Weight Materials
- Extenders
- Accelerators
- Retarders
- Lost Circulation Materials
- Special Additives

Figure 13a.

We have a number of additives for different purposes. We have additives to provide weight to the cement slurry, to extend its volume, to accelerate the setting of the cement, to retard the setting of the cement, to provide lost circulation control, and then there are special additives for special problems. (Figure 13b shown.)

Materials to Increase
Cement Slurry Weight
Sand
Barite
Hematite

Figure 13b.

Of the weighting materials, perhaps the most used is barite or barium sulfate. Hematite, an iron oxide, has been used; it is also a very heavy compound and can provide high density for the cement slurry. Sand too is used at times. These materials are ground to a powder form much like the cement solids so that they can be dispersed and transported through the system, to increase the density of the slurry.

Another way of getting the increased density is to add a dispersant to the cement slurry. A dispersant is a material that causes the cement to require less water to be pumpable; therefore we can use the cement solids themselves to increase the density. This this method we can get up to around 17-1/2 pounds per gallon without any extra inert materials. With combinations of the dispersant and these weighting additives, densities as high as 22 pounds per barrel have been obtained. (Figure 13c shown.)

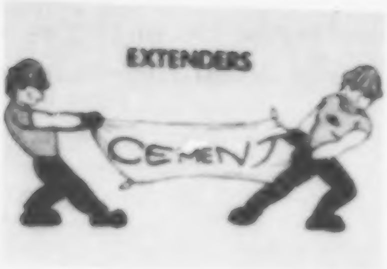


Figure 13c.

The extenders are materials that allow us to use extra water and reduce the density of the slurry or get a greater yield from the sack of cement. The yield from the sack of cement is what we are after in this case. And if we can obtain this cheaply, then these extenders are very valuable. Examples of extenders are usually the pozzalamic-type materials, such as volcanic ash or diatomacious earth, or the materials that we produce, such as fly ash from our plants. (Figure 13d shown.)

ACCELERATORS

Figure 13d.

Accelerators are used to reduce the time required for cement slurry to set into a hard mass, or to reduce the setting time. The best example is calcium chloride. It accelerates the setting of the cement considerably. It is used particularly in low temperature or shallow wells. (Figure 13e shown.)

Figure 13e.

On the other side of the scale we have retarders, in order to have enough working time with the slurry to allow us to set it in high-temperature wells. Retarders are lignin compounds or sugar compounds that retard the setting of this cement. It is an extremely difficult task to inject a cement slurry from the surface under 70° or 80° surface temperature down to the bottom of the well bore and back up and around the pipe, when the bottom hole temperature is 400° or 500° F, and have enough pumping time to get everything in place before it sets up. So the design of this cement, especially with the retarders, is extremely critical. (Figure 13f shown.)

Lost Circulation
Materials

Figure 13f.

Fine Sand
Antifoam Agents
Dispersants
Radioactive Materials
Fluid Loss Additives

Figure 13g.

In addition to materials that actually affect the reaction of the cement slurry, we have lost circulation materials, which are defined by their titles. They are to prevent lost circulation in cracks or in high permeable or vuggy formations so that the cement can be brought up around the pipe and not lost in the undesirable zones. Examples of this type of material are ground coal, known as kolite; gilsonite, which is a high-carbon material; and a flake-like material made of cellophane flakes. (Figure 13g shown.)

Special additives are also used for unusual problems. For example, in high temperatures, cement strength tends to degrade with time. So in an effort to control this cement loss, find sand is added to the cement slurry when temperatures get above, for instance 250° F.

At times we find we have a lot of foaming problems at the surface in trying to mix these cement slurries, so antifoam agents are added to help in the mixing operation.

Some dispersants are used, which, as we have already mentioned, allow us to use extra water.

Fluid loss additives are added, because as the cement slurry is passed across the face of a formation which has permeability and porosity, we tend to lose the water from the slurry. As this happens, the mixture becomes too thick to pump, and at times it could, in a sense, set up and not be pumpable, even though chemically it has not had time to react and form the solid mass that we usually consider cement.

There are many others too numerous to mention at this time. (Figure 14 shown.)

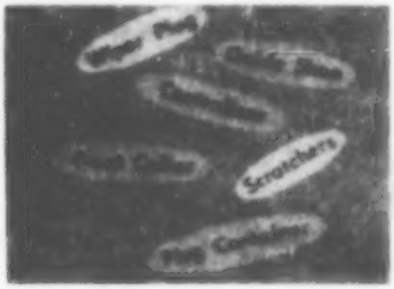


Figure 14.

When cementing casing in the well, there are some important pieces of equipment that could be called auxiliary equipment. These are not always used but they do have a definite purpose and should be used whenever possible. (Figure 15a shown.)

Figure 15a.

A float shoe is screwed onto the first joint of casing run into the well. This round-nosed device acts as a guide for the casing and prevents it from hanging on ledges as the casing is lowered into the well. The ball acts as a check valve and prevents the cement from coming back into the casing after it has been displaced. The float shoes are also made with a flapper valve in place of the ball.

Guide shoes are sometimes used instead of float shoes. Their main purpose is to guide the casing down the hole. They do not contain a valve mechanism.

The float collar shown has a spring-loaded flapper valve which allows fluid to pass through it from the top and closes similar to a bathtub stopper when fluid attempts to enter from the bottom. This allows the casing to be floated into the hole by the buoyancy of the partially filled casing. The float collar is usually placed one joint above the float shoe. Float collars are also made with the ball check instead of the flapper. (Figure 15b shown.)

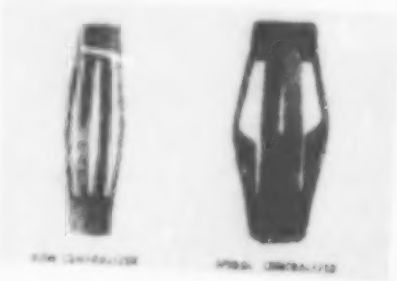


Figure 15b.

Centralizers are simply devices with bow springs similar to leaf springs on a car. These heavy spring steel guides fit around the outside of the casing and help center the casing in the bore hole during the cementing operation. Some operators prefer the spiral centralizer. It contains spiral blades which deflect the flow of fluid and generate turbulence to aid in displacing the drilling mud from the annulus. (Figure 15c shown.)

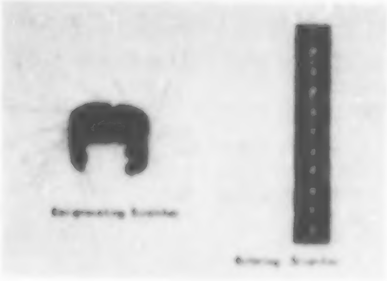

Reciprocating Scratcher
Rotating Scratcher

Figure 15c.

Scratchers are placed on the outside of the casing and are used to remove the mud from the formation face so that the cement will make a good seal against the rock. To get the proper action from the scratchers, the casing has to be moved up and down or rotated, which depends upon the type of scratcher used. (Figure 16 shown.)

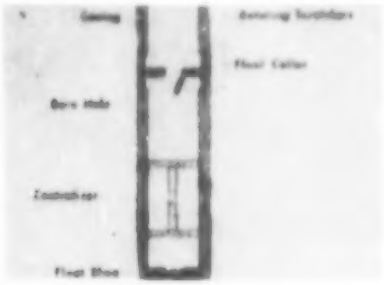

Casing
Rotating Scratchers
Float Collar
Bore Hole
Centralizer
Float Shoe

Figure 16.

Figure 16 illustrates the use of the four pieces of equipment previously discussed as they might be used in a well. The float shoe directs the centralized casing to the bottom of the bore hole. A fluid such as cement is free to move down the casing through the open flapper in the float collar and on to the bottom of the casing. As the cement passes through the float show, the centralizer holds the casing in the center of the bore hole, allowing the cement to completely surround the steel casing. The scratchers remove the drilling mud cake from the formation as the casing is rotated. (Figure 17 shown.)

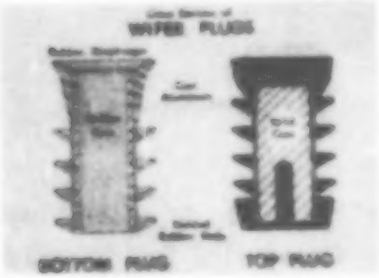


Figure 17.

Casing wiper plugs are designed to be run inside the casing ahead of and behind the cement slurry on a casing cement job. These plugs help prevent contamination between the cement and the drilling fluids as they move down inside the pipe. The plugs also help remove drilling mud that adheres to the inside of the casing.

In the past, wiper plugs have been constructed of materials such as gunny sacks, cast iron, leather, and wood. The present design calls for either cast aluminum or plastic cores with a molded rubber body.

The bottom plug, shown at the left in figure 17, has a hollow core with a diaphragm which is ruptured by increasing the fluid pressure on the plug after it has seated on the float collar. This plug allows more complete removal of mud from the casing and rupturing of the rubber diaphragm allows continued pumping after the plug seats on the float collar.

The top plug on the right has a solid core designed to completely close off fluid movement when seated on the float collar. (Figure 18 shown.)

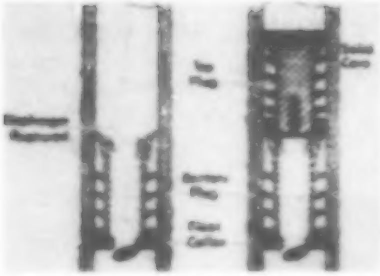


Figure 18.

Figure 18 illustrates the seating action of wiper plugs in the casing. On the left we see the bottom plug seated with the diaphragm ruptured and fluid being pumped through the casing. On the right the top plug has been pumped to the bottom stopping fluid movement through the casing. (Figure 19 shown.)

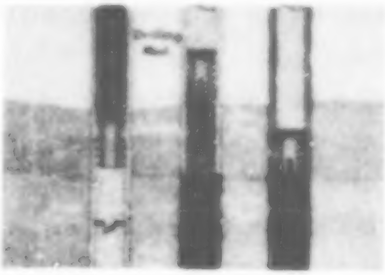


Figure 19.

This series of well sketches shows the fluid movement in the casing during a cement job. In diagram #1, mud is being circulated out of the pipe with the bottom wiper plug separating the drilling mud from the cement. In diagram #2, the bottom wiper plug has seated on the float collar and the diaphragm in the plug has ruptured, allowing the cement to move around the shoe of the casing and into the annulus. The top wiper plug is separating the cement and the drilling mud is used to displace the cement.

Diagram #3 shows the top wiper plug displaced to the shutoff point on the float collar, with cement left in the casing below the float collar and in the annulus.

Many factors go into the design of auxiliary equipment for casing, cement requirements, and cementing techniques. All of these factors can influence the success of a cement job. The oil operators, in conjunction with service companies, strive to apply the design factors necessary for the economic and successful primary cement job on each well. (Figure 20 shown.)

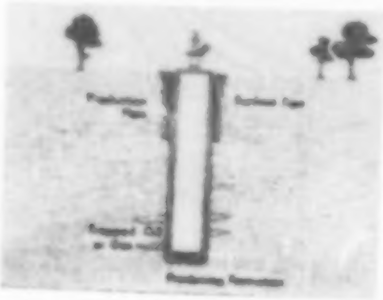


Figure 20.

Now let us refer back to our original diagram of the cutaway of the earth's surface showing the trapped fluid in the producing formation. The surface pipe has been placed in the hole and cemented. Production pipe has been run through the producing formation and the well is ready for completion work. The casing can now be perforated and the well can be tested. (Figure 21 shown.)

When we first perforate the well, bullets or jet charges are used to drive holes through the casing, thus giving us a contact with the formation into which we have drilled. Figure 21 shows one plane of four shots, one in each of the quadrants of the plane. Holes are shown through the casing and the cement, and out into the formation itself.

Chemicals are usually not involved with the perforating stage. However, at times chemicals are induced and spotted to bottom so that the perforation process will take place within a special chemical, one usually designed to give us less damage to the formation during the perforating

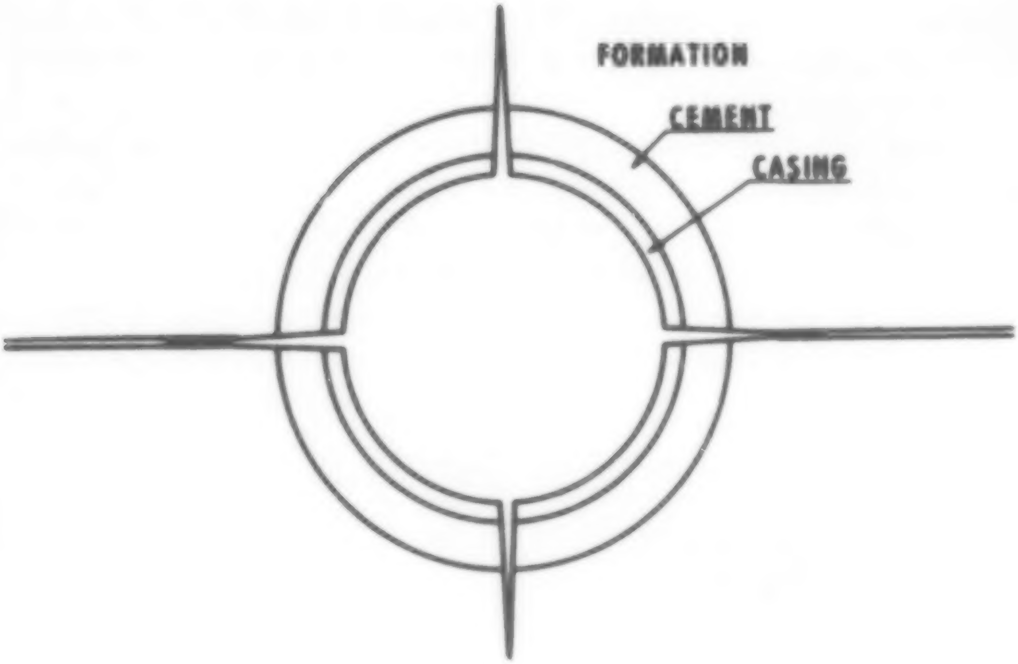


Figure 21.

stage. If you perforate in drilling mud you can damage the formation around the perforation and greatly restrict flow back into the pot. So organic acids or hydrochloric acids are sometimes used as perforating fluids.

After we have perforated, we will usually want to stimulate the well. This simply means to get the production rate up to a higher value than it would be naturally. It might be damaged at this point and stimulation may be necessary to get production up to an economical level. (Figures 22, 23, and 24* shown.)

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*Figures 22, 23, and 24 are courtesy of the Birdwell Division of Seismograph Service Corporation, Tulsa, Oklahoma.

Figure 22.

Figure 23.

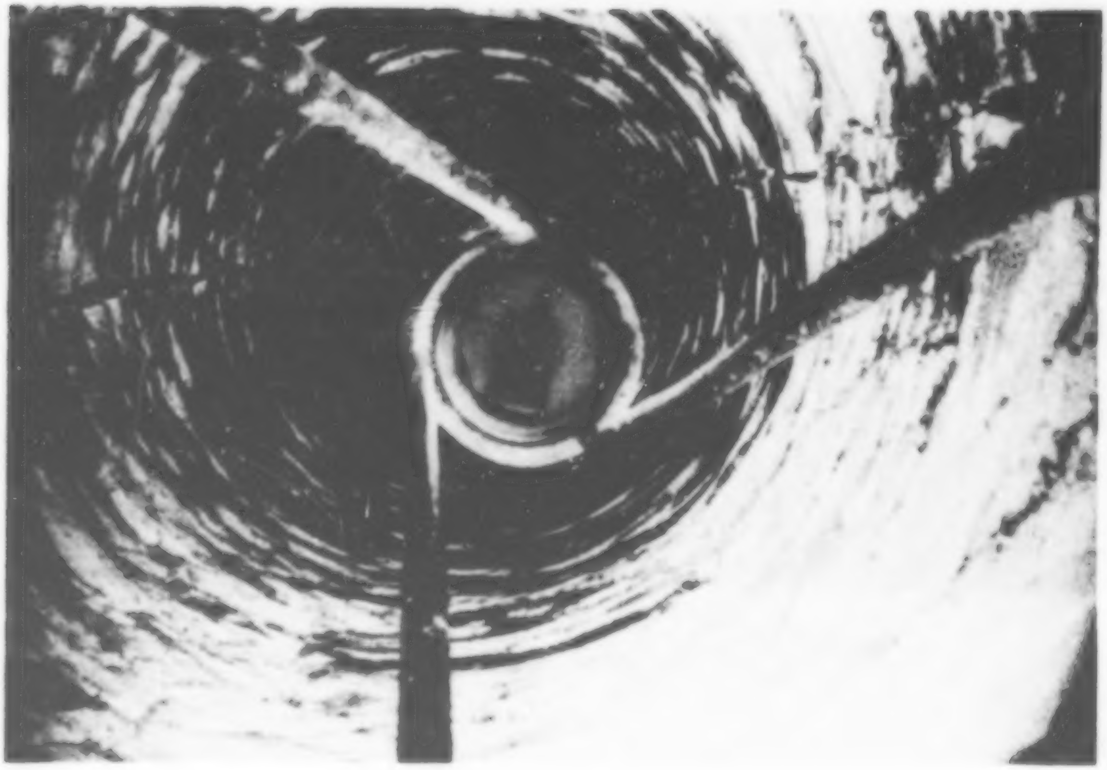


Figure 24.

Two methods have been used extensively for stimulation. These are fracturing and acidizing. I am going to try to cover these very quickly.

In fracturing we pump a water-base, oil-base, or acid-base fluid into the formation at a rate greater than it can accept; the resulting effect is that high pressures are created, and the formation is cracked or parted by the high pressure creating the fracture. To show what this might look like, Figure 22 is a down hole picture of an open hole completion, (no casing across the producing zone) prior to fracturing. Following a fracturing job we see a vertical fracture across the same interval (figure 23). You can take pictures, if you happen to have a gas well where fluids do not interfere with the picture taking operation. By hanging a compass below the camera, we can determine the orientation of this fracture (figure 24). We usually find that the fractures are vertically inclined and extend in opposite directions from the wellbore, as shown in these three figures.

The same type of fracture occurs outside our perforated casing. We obviously cannot see it but we have means of detecting the fracture.

The fracturing principle, then, is one of driving a wedge of fluid into the formation, creating a vertical fracture, and extending it out some distance so that we can make this formation produce at a much higher rate than normally would be expected considering fluid properties, the permeability, and pressures that are involved.

The size of fracturing treatments varies greatly, from a few thousand gallons of fluid to the largest jobs of over a million gallons of fluid pumped while fracturing the formation. The fractures can be extended to several thousand feet into the formation. The massive fracturing treatments being performed today are designed for 2,000 feet of penetration in each direction from the well.

The fracture that we have created, is propped open by fracturing sand that is carried in with fracture fluid. It acts as a wedge to hold the fracture open and provides a highly conductive channel from the reservoir in the formation back to the wellbore. This is illustrated in figure 25. (Figure 25 shown.)

The surface equipment used in fracturing is quite extensive, very complicated, and very expensive. (Figure 26 shown.) In figure 26 we see a frac treatment using six pump trucks and three blenders, one blender to each pair of pumpers, and sand trucks dumping sand into each blender. There are three separate units shown here. Each blender picks up the fracturing fluid that is stored in the tanks, adds the sand to it, and with a centrifugal feeds the frac fluid-sand slurry to two high-pressure pumpers. The high-pressure pumps in turn pump the mixture down the pipe and out into the formation. This would represent a typical size treatment. (Figure 27 shown.)

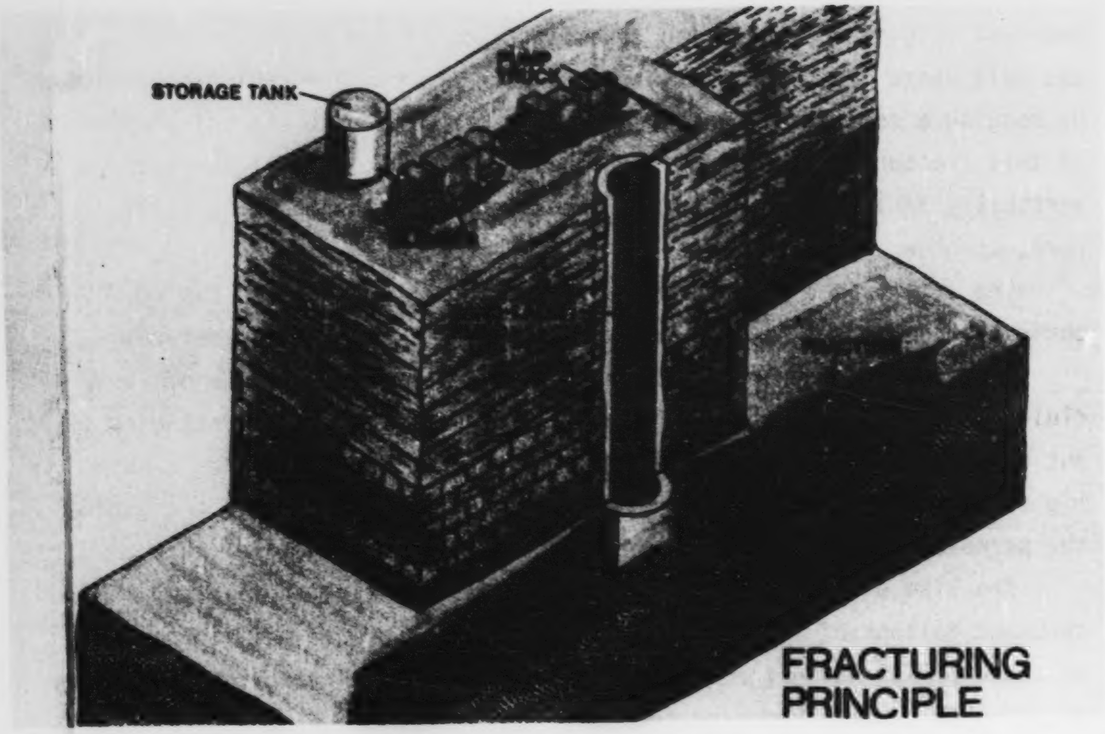

STORAGE TANK
FRACTURING PRINCIPLE

Figure 25.

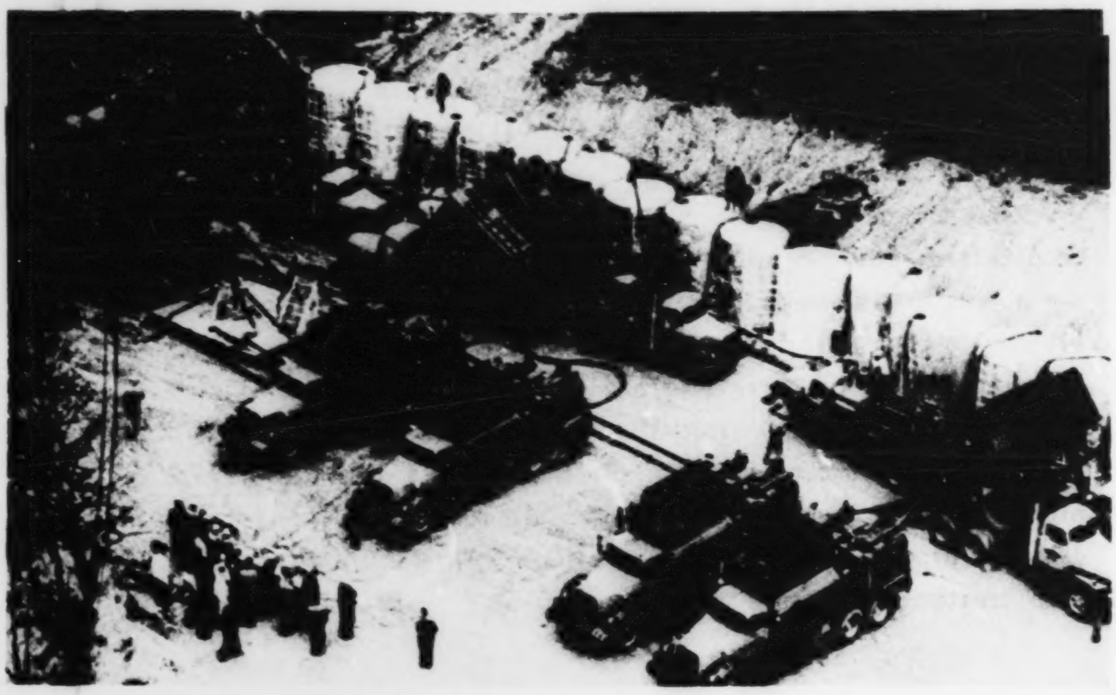


Figure 26.

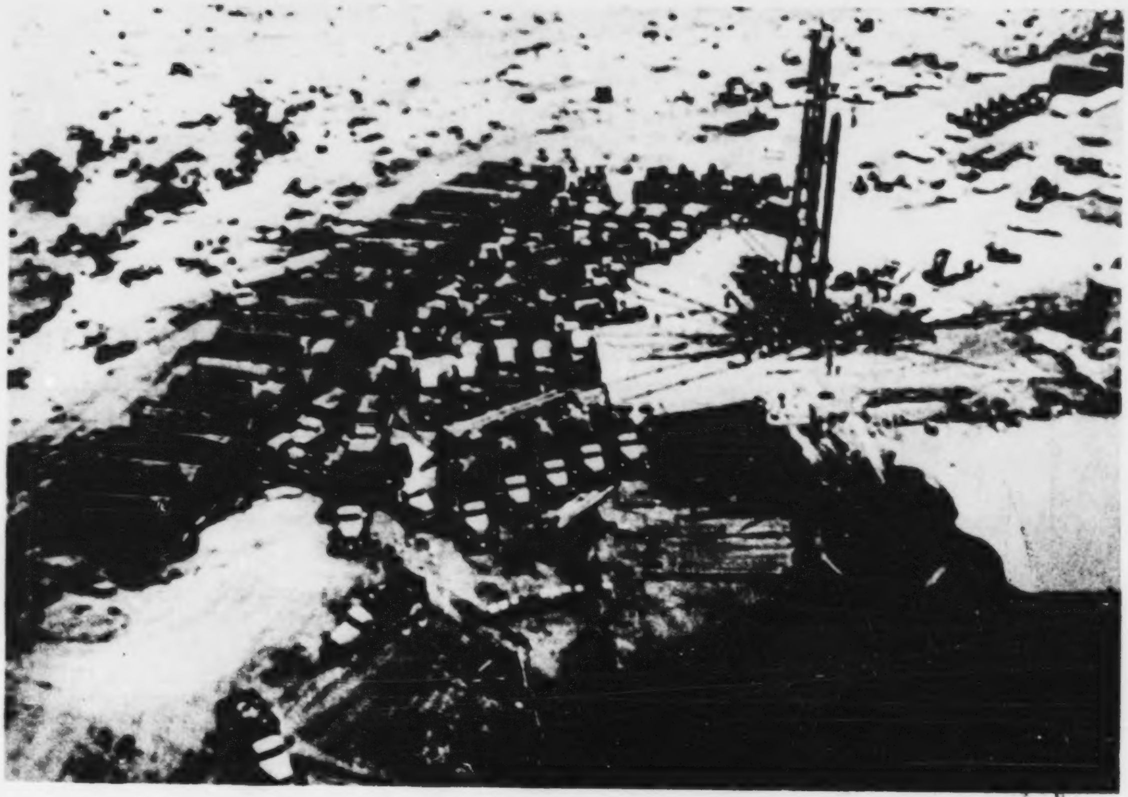


Figure 27.

Every so often we have massive jobs, where there might be 12 to 24 of the high-pressure pumps going. Figure 27 shows a large or massive frac treatment. A considerable amount of investment is involved in doing a job such as this, since each pump truck today probably costs on the order of a quarter of a million dollars by the time you get it equipped and on location. In this case, very large tank storage is required to hold the large volumes of fluid, and many sand trucks are needed to haul the sand. (Figure 28 shown.)

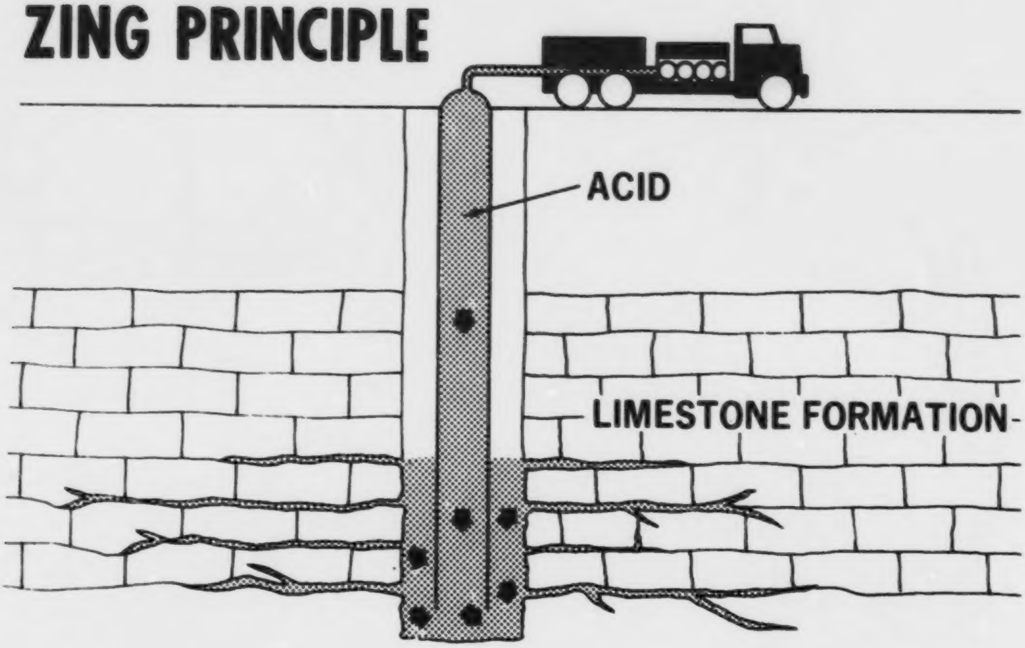
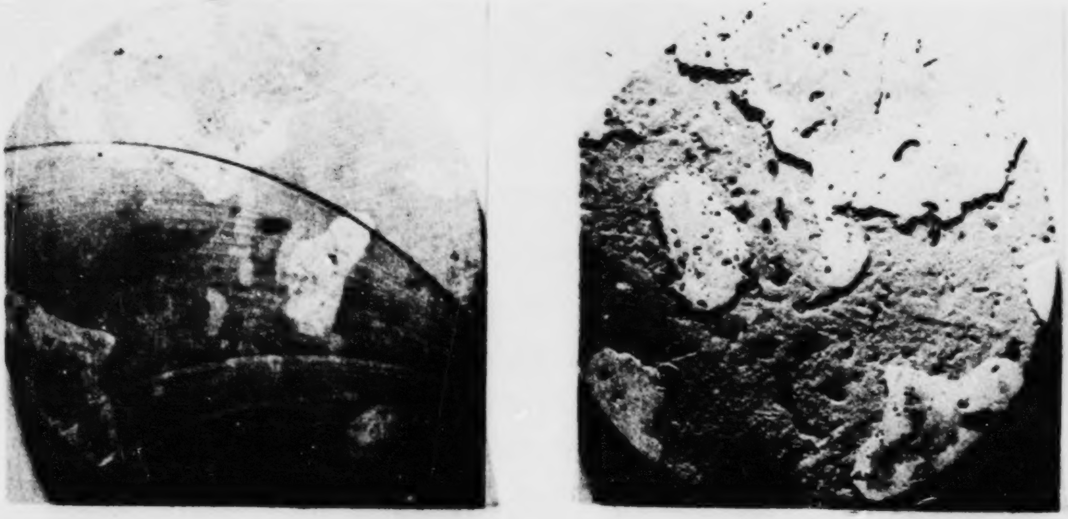

ZING PRINCIPLE
ACID
LIMESTONE FORMATION

Figure 28.



FRACTURE FACE BEFORE ACIDIZING

ACIDIZED FRACTURE FACE

Figure 29.

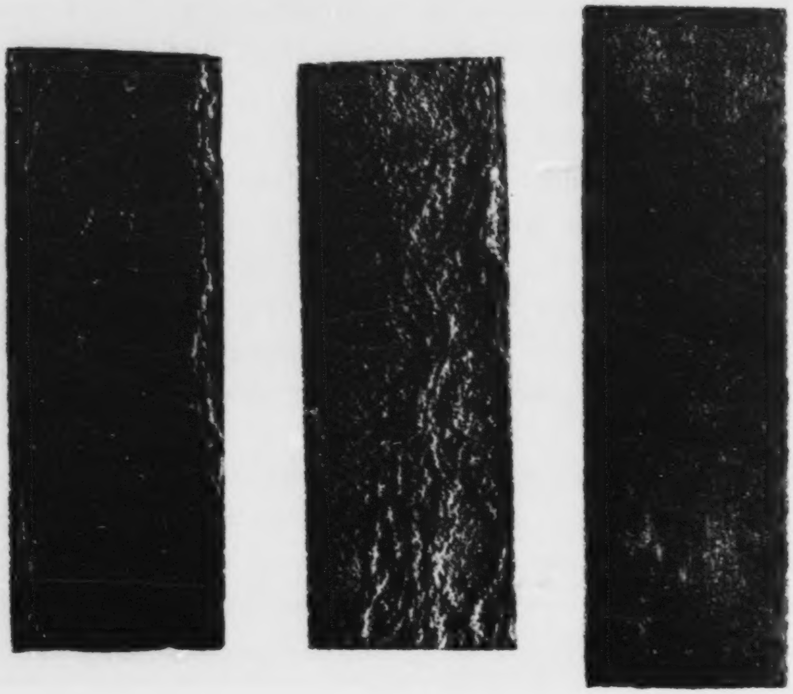


Figure 30.

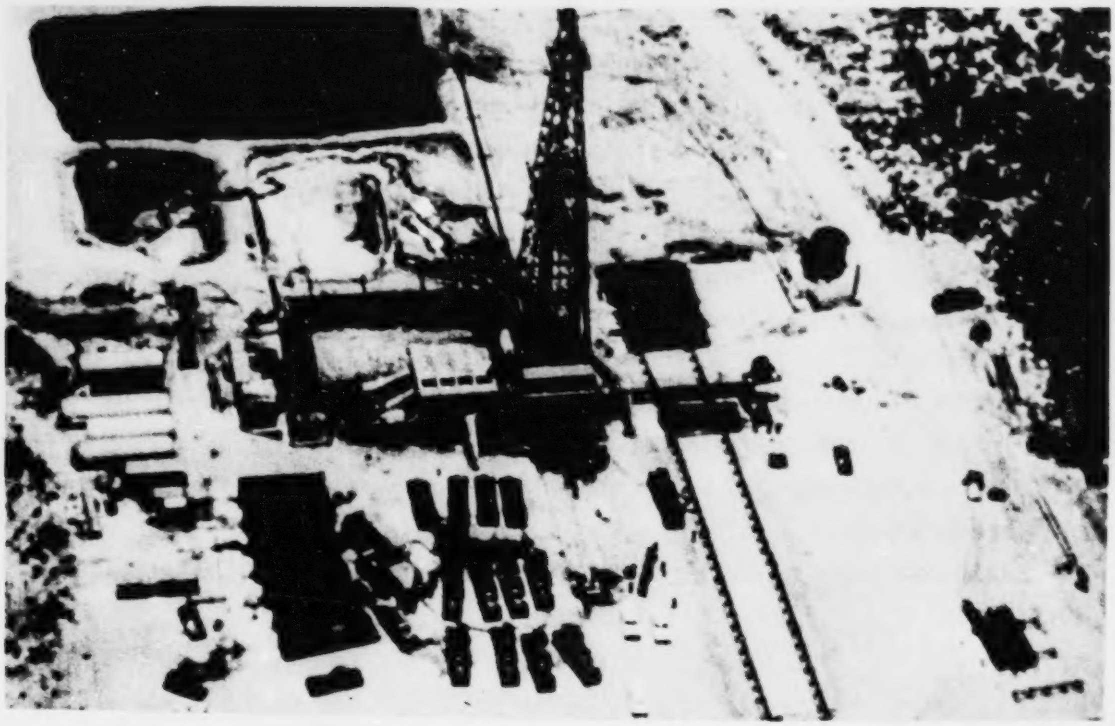


Figure 31.

The other method of stimulation is acidizing, which is done one of two ways. The acid is injected at a high rate and pressure so that the formation fractures, or it is injected at a low enough rate and low enough pressure to force the acid into the pore structure of the producing formation, thus improving the draining pattern (permeability) into the wellbore from the formation itself.

In the case of acidizing at a high injection rate, we are creating a hydraulic fracture as in a frac treatment, only rather than propping it open with sand, the acid dissolves the limestone into which we are injecting that acid and leaves channels along this fracture pathway to provide for conductivity.

If we take cores from the limestone formation and look at them, we find that they are not perfectly pure limestone; there are insoluble materials and there are some very dense areas of limestone that dissolve at a different rate. In passing acid over the face of this limestone we get an irregular etched face as shown in figure 29. (Figure 29 shown.) This helps provide an open fracture with high conductivity after the acid job. (Figure 30 shown.)

Figure 30 shows the effect of running acid over the face of a rather pure limestone sample (panel at right). In the center panel, 15 percent hydrochloric acid was passed across the face and you can see the etched channels. On the panel at the left, 28 percent hydrochloric acid is passed across and more deeply etches the surface. At any rate, between flow characteristics and the impurities and insolubles across the face of a hydraulic fracture, in limestone or dolomite, we get an uneven etch pattern. This pattern provides the highly productive channels out into the formation and the fluid--such as petroleum--can passs easily through this channel back to the wellbore and up to the surface. (Figure 31 shown.)

Figure 31 shows a large-volume acid treatment being performed in West Texas. A large tank volume is required to hold the large volume of acid and displacement fluid. Blenders pick up the acid and feed the high-pressure pumpers.

That concludes my rather brief discussion on the well completion techniques.

21 May 1975

Session I: (con.)

TECHNIQUES AND CHEMICALS USED IN WELL DRILLING

James L. Lummus
Chairman

TOXICITY STUDY
DRILLING FLUID CHEMICALS ON AQUATIC LIFE

C. K. Grantham and
J. P. Sloan*

Abstract

Weighting materials have been added to drilling fluids since early in the twentieth century, and the potential environmental impact of the introduction of these additives as industrial compounds is one of contemporary concern. This paper investigates the toxicity of density building materials used in drilling mud; it reviews the nature and purposes of these additives; and it generally discusses results of toxicity tests conducted on the weighting materials used in drilling fluids. General comments correlating other industrial or professional applications, where possible, are indicated to clarify comparisons of relative safety or toxicity for humans.

INTRODUCTION

Of the various functions of drilling muds, controlling subsurface pressures is probably the most crucial. When high pressure zones are penetrated, the hydrostatic head of the mud column must be sufficient to offset the varying subsurface pressures. Consequently, drilling fluid densities must vary from 8.3 to 22.0+ pounds per gallon. These weights are attained by adding finely ground high density materials such as barium sulfate, calcium carbonate, and iron carbonate.

Although compounds used to weight drilling fluids are naturally occurring minerals, ubiquitous within the earth's crust and found in virtually every living creature, it is not current practice to dispose of expended drilling fluids into the environment. Rather, drilling fluids are retained as a wellbore packing, treated in holding pits, or retrieved

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for later use. This study examines the environmental effects of these minerals additives to determine if they represent a harmful or toxic impact upon marine life.

Today, barite (barium sulfate) is by far the most common additive employed in drilling fluids. It is inert in alkaline, acid, and neutral solutions, soft, clean, low in cost, has a high density, and is commercially available worldwide. Two other weighting materials that are used (less frequently than barite) are calcite (calcium carbonate) and siderite (iron carbonate). Because of the acid solubility, they are used in oil muds and brines to give density to workover, completion, and perforating fluids.

BARITE

In drilling fluids, barite accounts for 98 percent of weighting agents used. World production in 1974 was 4.7 million short tons (ref. 1). Of this, 83 percent was used in drilling fluids.

The physical and chemical properties of oilfield barite must meet specifications adopted by the American Petroleum Institute (API) concerning density, particle size, and chemical hardness. Primary API quality barite deposits are found in Battle Mountain, Nevada, and Potosi, Missouri. Smaller deposits are mined and processed in Alaska, Arkansas, California, Georgia, Idaho, Illinois, and Tennessee. In addition to domestically produced barite, imported barites from 12 other countries are used in drilling fluids. Some are processed as received, while some are blended with domestic barites to provide a more uniform product. Barite-weighted fluids can be formulated to approximately 22 pounds per gallon.

In barite, the percentage of purity varies between deposits. However, most of the impurities found in crude barite are removed after grinding and crushing by mechanical (jigging) and chemical (flotation) processes which function on differences in specific gravity. The primary contaminants which remain in all finished barite are silica and iron compounds; in Battle Mountain barite it is silica; in Potosi it is iron oxide; in imports from Ireland it is iron compounds; and in Greek-produced material it is iron oxide.

CALCITE

Calcite is in limited use today. In 1974, approximately 3,000 tons were sold for weighting drilling fluids. Calcite's uses are limited [because of the mineral's low specific gravity (2.7)] to mud weights of less than 14 pounds per gallon. It is most often used in workover or completion fluids for normally pressured formations and depleted or drawn-down reservoirs. Its complete solubility in hydrochloric acid in contrast to barite insolubility makes it very desirable for this application instead of barite. Therefore, only the purest grades of limestone are selected for oilfield application.

SIDERITE

Within the last 2 years, siderite has been introduced as an acid-soluble weighting material for workover and completion fluids. Siderite can be used where mud weights between 14 pounds per gallon and 18 pounds per gallon are required. Also, lower mud weights are sometimes formulated by mixing siderite with calcite. Siderite, like calcite, is desirable as a weighting material because of its solubility in hydrochloric and formic acids, and its specific gravity (3.8) is higher than calcite.

ANALYSIS

This analysis considers effects of water soluble constituents of barite, calcite, and siderite on the *potential impact* on marine life.

In this study, dissolved constituents were differentiated from suspended metals by filtering all solutions through a 0.2-micron millipore filter. Results of the analyses indicated that each additive was inert and exhibited no appreciable water solubility.

A typical analysis of the water soluble ions present in commercial Battle Mountain, Potosi, Greek, and Irish barite is given in table 1. In tables 2 and 3, typical analyses of calcite and siderite illustrate that these minerals, like barite, are inert and exhibit no appreciable water solubility. Generally, elements found to be inert and insoluble in water are not considered to be toxic upon aquatic life.

Table 1. Compositional analysis of drilling mud grade barium sulfate (barite)

Properties	Battle Mountain	Potosi	Irish	Greek
Specific gravity	4.24	4.31	4.34	4.13
Barium sulfate	90.8	80.4	86.3	67.7
pH	7.5	7.0	7.2	7.0
Water solubles*	mg/liter	mg/liter	mg/liter	mg/liter
Calcium	1	20	48	30
Magnesium	.8	10	22	10
Sodium	120	20	190	140
Potassium	0	1	18	7
Barium	0	0	0	0
Copper	0.2	0	0.1	0.1
Zinc	0.1	0.1	0.05	0.05
Lead	0	0	0	0
Manganese	0.05	0.1	0.1	0.2
Bicarbonates	200	90	40	50
Carbonates	50	10	5	10
Hydroxides	0	0	0	0
Sulfates	80	70	400	160
Chlorides	60	30	50	190

*Obtained after filtering through a 0.2-micron millipore filter.

Table 2. Compositional analysis* of drilling mud grade calcium carbonate

Properties		Water solubles*	
Specific gravity	2.7	Calcium	160
pH	8.3	Magnesium	0
Calcium carbonate (calcite)	93.6%	Sodium	15
SiO_2	5.7%	Potassium	0
Fe	.05%	Bicarbonate	730
		Hydroxide	0
		Carbonate	0
		Sulfates	0
		Chloride	50

*Obtained after filtering through a 0.2-micron millipore filter.

Table 3. Compositional analysis* of drilling mud grade iron carbonate (siderite)

Properties		Water solubles*	ppm
Specific gravity	3.75	Calcium	8
pH	6.00	Magnesium	0
Iron carbonate ($Fe(CO_3)_2$)	90.0%	Iron	0
Hematite (Fe_2O_3)	3.0%	Sodium	2
SiO_2	5.0%	Potassium	5
Calcium carbonate	2.0%	Bicarbonates	7
		Hydroxide	0
		Carbonates	0
		Sulfates	44
		Chlorides	10

*Analysis performed after filtering through a 0.2-micron millipore filter.

In our study of the literature, we have noted that barite, calcite, and siderite are used frequently for varied industrial and professional purposes, including use as medicinal compounds for human consumption. Barium sulfate is widely employed as a contrast medium for roentgenographic purposes and as an antidiarrheal and demulcent powder (ref. 2). These medicinal compounds are administered routinely by medical doctors as internal medicine.

Calcium carbonate (calcite), specifically used as a gastric antacid and antidiarrheal, is widely included in the formulations of dentifrices, cosmetics, pharmaceuticals, and foods (ref. 3). Iron carbonate (siderite) is used in formulations which are ingested directly by humans and animals. Iron carbonate also has been prescribed to treat iron deficiency anemia, and it is used as a food supplement in cattle feed (ref. 3). Iron carbonate has GRAS status in the Federal Food, Drug, and Cosmetic Act, under Food Additive Amendment GRAS 121.101 (f) (NCR No. 6-01-863).

In the geosphere, barium is the sixth most abundant trace element and is ranked as the 17th most abundant crustal element, representing 400 ppm (ref. 4). In water, the natural barium content of rivers ranges from 0.007-15 ppm (ref. 5); in a survey of the 100 largest U.S. cities, barium in municipal waters is found to average 43 ppb, varying between 1.7-380 ppb (ref. 6).

Barium is found in all forms of life (ref. 7) and is present in human organs from birth. Man's skeleton itself contains an average of 2 ppm barium, muscles and lungs contain 14 ppm, and human blood plasma contains 79 ppb barium. It is estimated that humans ingest 1.33 mg of barium daily while excreting an equivalent amount (ref. 8), resulting in a stabilized, not cumulative, presence of barium.

Most marine life, both plant and animal, will contain higher concentrations of barium than their environment (ref. 9). Marine plants concentrate barium 1,000 times and marine animals from 7 to 100 times. Certain life forms--for example, the exoskeleton of the rhizopod xenophyofera--are made up largely of barium sulfate (ref. 8). Insoluble barium sulfate is tolerated by all species, and a barium meal or enema may amount to 0.5 percent of the body weight (ref. 10).

TOXICITY TESTS

To study the toxicity of barite, calcite, and siderite, an independent research firm was commissioned to conduct standard fish toxicity tests. Fish were the logical life form because they are the most direct link between water and marine life. Our toxicity studies, performed according to the Acute Fish Toxicity Test of the American Public Health Association (APHA), show that heavy concentrations of barite, calcite, and siderite exhibit no toxicity to fish. In this standard toxicity procedure, *Mollienisias latipinna* (mollies)--a medium tolerant fish adaptable to both fresh and salt water--were exposed to concentrations of chemical additives up to 100,000 ppm for 96 hours. (Any higher concentrations of the weighting material are considered a measure of the concentration and not the toxicity).

From the results of these fish toxicity tests, we conclude that barite, calcite, and siderite in concentrations up to 100,000 ppm introduced into fresh or sea water do not constitute a toxic environment (tables 4,5,6).

CONCLUSIONS

The toxicity and environmental impact of any material is necessarily evaluated on the basis of its availability for reaction. Barite, calcite, and siderite used as drilling fluid additives are present as insoluble metal salts. Further, they are naturally occuring materials with a wide

Table 4. Acute fish toxicity test barium sulfate (barite)

Concentration in sea water & fresh water ppm	No. of test animals*	No of test animals surviving		
		After 24 hours	After 48 hours	After 96 hours
100,000	10	10	10	10
50,000	10	10	10	10
0	10	10	10	10

**Mollienisias latipinna*.

Table 5. Acute fish toxicity test calcium carbonate (calcite)

Concentration in sea water & fresh water ppm	No. of test animals*	No. of test animals surviving		
		After 24 hours	After 48 hours	After 96 hours
100,000	10	10	10	10
50,000	10	10	10	10
0	10	10	10	10

**Mollienisias latipinna*.

Table 6. Acute fish toxicity test iron carbonate (siderite)

Concentration in sea water & fresh water ppm	No. of test animals*	No of test animals surviving		
		After 24 hours	After 48 hours	After 96 hours
100,000	10	10	10	10
50,000	10	10	10	10
0	10	10	10	10

**Mollienisias latipinna*.

distribution throughout the earth's crust and whose cations are present in man from birth to death, although they are not retained by the body above required levels.

Both marine animals and plants naturally concentrate barium from sea water in levels several times that of the water. Results of fish toxicity tests conducted indicated that barium sulfate, calcium carbonate, and iron carbonate are not toxic to fish in either fresh water or sea water. Therefore, it can be reasonably concluded that the use of these weighting materials in drilling fluids do not constitute the introduction of a toxic substance into the environment.

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DISCUSSION

DR. ELLIOTT S. HARRIS (NIOSH, CDC, DHEW, Cincinnati, Ohio): The levels that you gave--100,000 parts per million, which is equivalent to about 10 percent--seem to me to exceed the solubility of most of the compounds that you were talking about.

MR. GRANTHAM: Right, they do.

DR. HARRIS: It seems, then, that you are dealing with a saturated solution in each case, no matter what your apparent total levels are. Do you have any idea what those were, because that is really the concentration that you are concerned with?

MR. GRANTHAM: I'm not sure when you say ". . . what those are." What are the saturation levels?

DR. HARRIS: What were the concentrations that you were truly dealing with? 100,000 parts per million is equivalent to 10 percent. You are talking about 10 percent. I doubt if you would have a 10 percent solution of any of those compounds; you are dealing with a sludge or a slurry.

MR. GRANTHAM: Right.

DR. HARRIS: All right. I am asking what the concentrations of calcite, siderite, and barite were in solution in each of those tests you ran, because it is the solution concentration that you are concerned with in toxicity tests.

MR. GRANTHAM: Right. I could probably put 1 gram in the sample and have it saturated because of the solubility of these particular minerals. So that is what I was saying earlier. At concentrations of 100,000 parts per million and above, we are just talking about a concentration effect, not a toxic effect. Any toxic material would have saturated these concentrations. There were no toxic effects.

DR. HARRIS: Was any pathology done on the fish at the end of the results?

MR. GRANTHAM: No, there was not.

DR. HARRIS: Thank you.

DR. RICHARD S. SCALAN (University of Texas, Marine Science Institute, Port Aransas, Texas): I have a comment to make which would perhaps lead to some discussion later. Such organisms as the mollie, a large fish, or a shark are not the important organisms in the sea.

In fact, the major bio-mass lies in the single-cell organisms called phytoplankton. Probably the most toxic things that you could find about your drilling mud compositions would not be those which are soluble but, indeed, those which are insoluble because these increase the turbidity of the ocean. From an operating rig, there issues a big long plume of material; whether this is drilling mud or particulates or just what, I am not sure. It is this turbidity that is going to cut down the amount of light in the ocean, and it will thus force these organisms, which depend upon light (photosynthesis is their main process) to come up to a higher level. So I would suggest that perhaps something for the panel to discuss would be, what would be the effects of turbidity on these important organisms.

CHAIRMAN LUMMUS: Thank you for the suggestion. We will have a panel discussion after the first three papers when we will review, recapitulate, and take care of this. Then we can talk about that.

FISH TOXICITY OF DISPERSED CLAY DRILLING MUD DEFLOCCULANTS

J. W. Hollingsworth and R. A. Lockhart*

Abstract

This paper investigates thinning agents used in simple sodium montmorillonite drilling fluids to deflocculate clay particles and maintain proper gel strengths. Thinning agents (phosphates, tannins, special lignites, and lignosulfonates) stabilize clay dispersion by preventing strong particle association and by decreasing the energy needed to initiate and maintain system flow. The paper describes the application of these thinning agents and reports the results of acute fish toxicity tests.

INTRODUCTION

Chemical-treating agents are added to drilling muds to control and stabilize the dispersion rheology for optimum solids carrying capacity and viscosity. Phosphates, tannins, special lignites, and lignosulfonates characterize the materials used commercially for this purpose in the dispersed clay water-base drilling mud system. This paper describes the application of these thinning agents (deflocculants) and reports the results of acute fish toxicity tests.

The dispersed clay drilling mud system was selected for investigation because it is one of the most widely used water-based drilling fluids. The principal components of this system are fresh water, sodium montmorillonite, and one or more chemical agents for rheology control. Additional materials are added to the basic system as required to obtain properties for different drilling conditions.

Thinning agents are required for use in simple sodium montmorillonite drilling fluids for two major reasons. Firstly, clay particles will

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flocculate and aggregate in the presence of electrolytes or elevated temperature and lose their effectiveness, and secondly, excessive and progressive gel strengths are generated by the strong electrical particle association formed when the fluid is static. Low fragile gel strengths are desirable in a drilling fluid to support weight material and cuttings when the fluid is not being pumped. However, as high gel strength develops, excessive pressure is required to induce flow, often causing formation damage and lost returns. These limitations are overcome by controlling and stabilizing the dispersion rheology with thinning agents which are modifications and salts of four compound types: phosphates, tannins, special lignites, and lignosulfonates. (Our estimate of total industry consumption of these agents in the United States, projected for 1975, is indicated in figure 1.)

These agents stabilize a montmorillonite clay dispersion by preventing strong clay particle association and decreasing the energy to initiate and maintain system flow.

PHOSPHATES

Although numerous phosphate salts and organo-phosphates have been employed as dispersed clay drilling mud thinners, at the present time only three types are commonly used: sodium acid pyrophosphate, sodium tetraphosphate, and sodium hexametaphosphate. At low concentrations, these dehydrated phosphates are effective thinners for fresh water sodium montmorillonite dispersions. Normal field dosage is between 0.1 and 0.5 pounds of phosphate salt per barrel of drilling mud.

The rheological response of a sodium montmorillonite dispersion treated with sodium acid pyrophosphate (figure 2) is typical of thinner treatment in general, and in particular of all phosphate salts. Apparent viscosity is reduced substantially and gel strengths are controlled in a desirable range. For this demonstration, no effort was made to adjust pH, although alkaline agents usually are added to dispersed clay drilling muds to increase the thinner activity and control corrosion problems associated with low pH. The phosphate-thinned mud pH is controlled to 7-8.5.

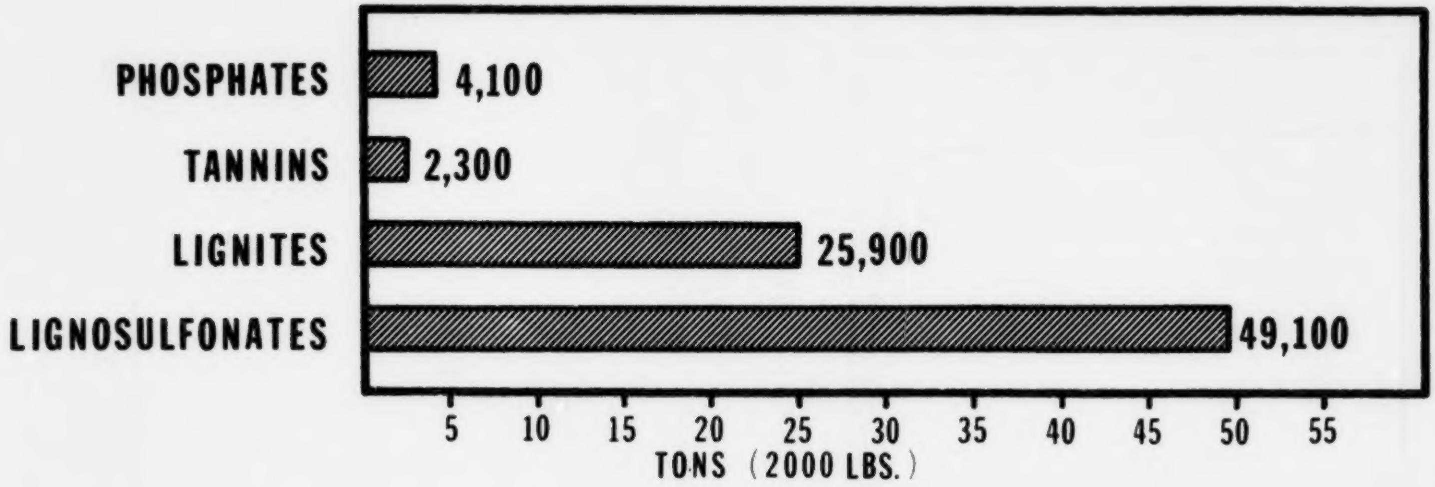


Figure 1. U.S. consumption of thinning agents for dispersed clay drilling muds (projected for 1975).

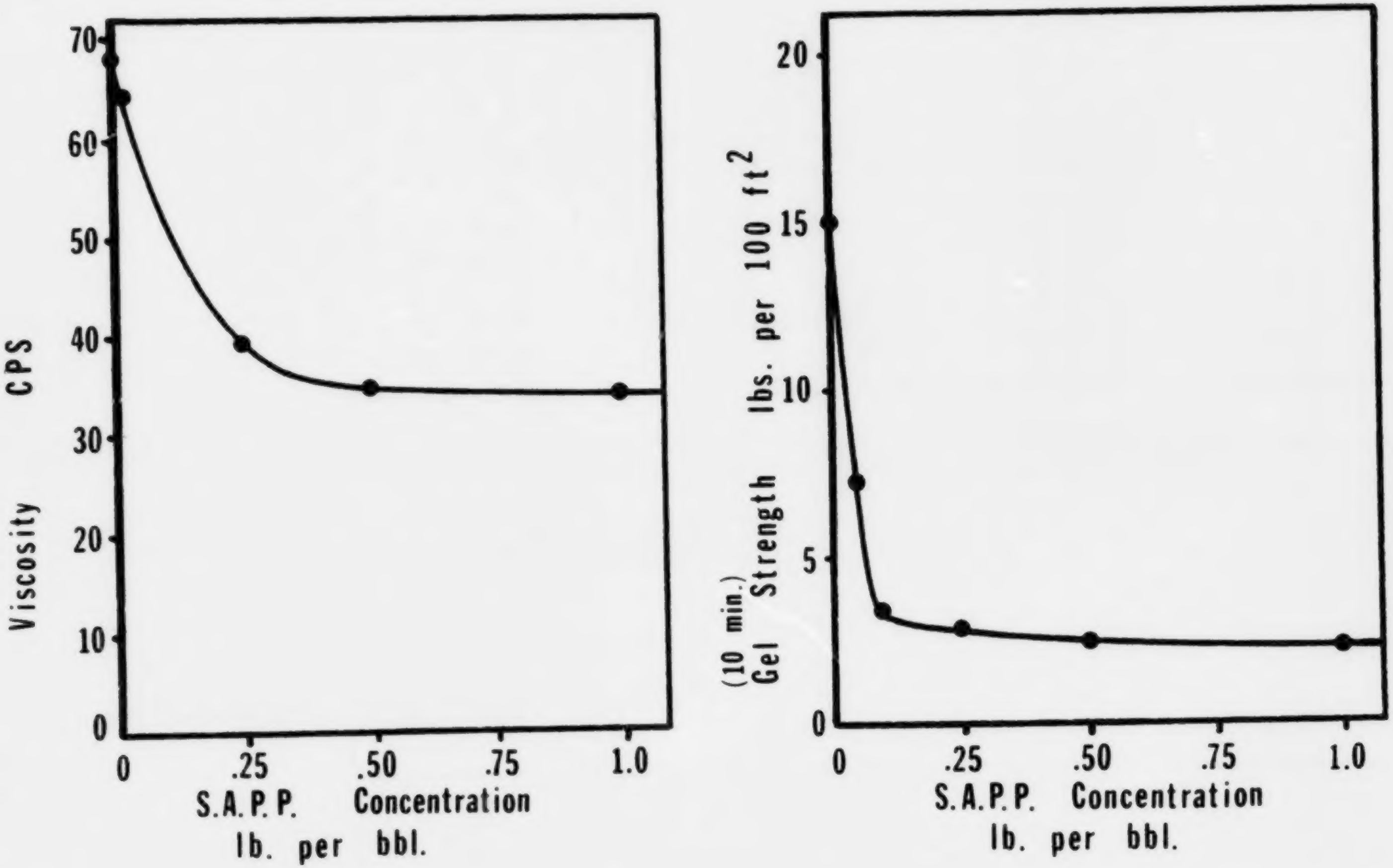


Figure 2. Rheological properties of a 25-lbs-per-bbl sodium monmorillonite dispersion treated with sodium acid pyrophosphate.

Dehydrated phosphate thinners are limited to low temperatures (below 200° F) and to fresh water applications because of their tendency to revert to ortho phosphates, especially at elevated temperatures. Thinning control is lost and insoluble salts formed if calcium contamination occurs. Often phosphates are employed in muds for reducing fluid hardness.

TANNINS

Tannin compounds are acidic organic substances extracted from various plants, including the quebracho, wattle, mangrove, hemlock, and redwood trees. Like the phosphate thinners, numerous tannins and tannin blends have been widely used as dispersed clay mud thinners. These materials were more prevalent before the advent of lignite lignosulfonate mud systems used today. Tannin agents require a high pH for optimum performance and lack adequate thermal stability for drilling today's deeper wells. However, their electrolyte contamination tolerance is superior to the phosphate compounds, and their oxygen scavenging ability is often utilized to combat oxygen corrosion problems.

Tannin agents are used in much higher concentrations than phosphates for drilling mud rheology control. The amount necessary to stabilize drilling mud rheology is a function of numerous variables, but will be dependent largely on the system's hydratable clay mineral concentration. A concentration of 2-10 pounds per barrel of tannin compound is a typical field mud requirement.

LIGNITE

Lignite for treating drilling mud is mined principally in North and South Dakota and differs from normal or fuel grade lignite in its high humic acid content and caustic solubility. (The optimum weight ratio of caustic to lignite in fresh water muds is approximately one to eight.) Lignite is sometimes used alone with sufficient caustic for solubility, but more often in conjunction with other thinners. Mixtures of lignites, alkalies, and/or tannins, as well as sulfonated, sulfomethylated, and metal chelated lignites have all been used successfully for treating drilling muds.

Drilling mud grade lignite is a polymeric humic acid with a complex and extremely variable organic structure containing about 10 percent inorganic inert solids. Lignite and its various derivatives are normally used in concentrations from 2 to 12 pounds per barrel of drilling mud.

Lignites demonstrate extreme thermal stability. Drilling muds using lignite/caustic for rheology control may be prepared that are capable of withstanding 300° F over extended periods and 400° F for a short time (16 hours). Unfortunately lignite/caustic solutions are subject to electrolyte sensitivity, and are precipitated by calcium contamination. Chemically modifying lignite often improves its electrolyte tolerance, but fails to prevent precipitation. Precipitated lignite usually continues to function as a fluid loss additive although its thinning properties are absent.

LIGNOSULFONATES

The lignosulfonate category includes simple lignosulfonate salts, such as calcium or sodium lignosulfonates, and the modified or complexed chromium and ferrochrome lignosulfonates. Simple lignosulfonates are used infrequently as emulsifiers and for treating specialized lime-caustic muds. Modified lignosulfonates are the most widely used and versatile thinning agents available today. They possess good electrolyte tolerance, work well over a wide pH range, withstand most drilling fluid levels of calcium contamination, and have exceptional thermal stability. They are routinely used in water-base drilling muds at concentrations varying from 2 to 10 pounds per barrel, to temperatures approaching 400° F.

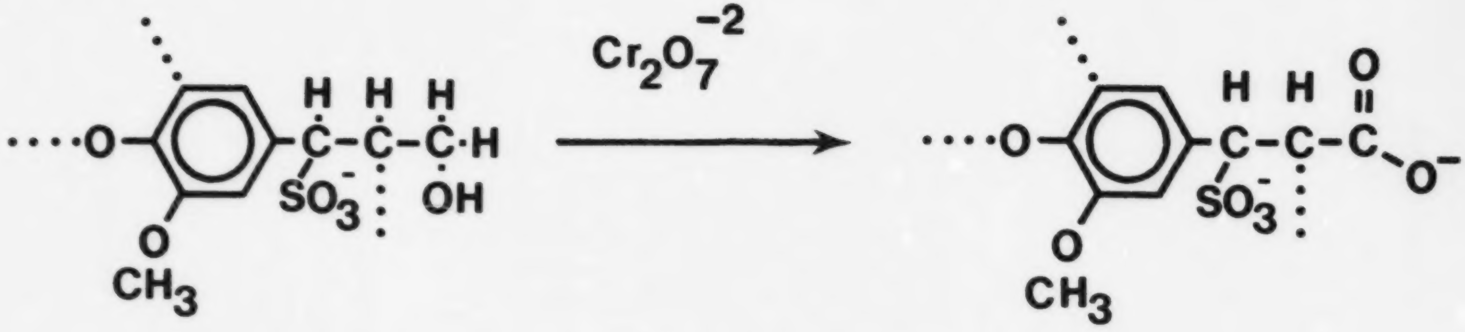
Both chromium (CLS) and ferrochrome (FCLS) lignosulfonates, the most commonly used deflocculants, are prepared by the dichromate oxidation of sulfite pulp lignosulfonate liquor. Earlier paper manufacturers routinely burned these components for their minimal fuel value, while others were issued permits to discharge excess quantities in plant waste water streams. The use of lignosulfonates as a valuable chemical component in drilling muds virtually eliminated this waste.

The lignin and lignosulfonate precursor of the modified CLS and FCLS products have been studied extensively. Lignin is a natural polymer recovered from wood in paper pulping operations probably originating from phenylpropane monomers. The most predominate lignin monomer is coniferyl alcohol. Polymerization and cross-linking occur at any number of possible sites to add to the complexity of the material. The sulfite pulping process preferentially sulfonates the alpha carbon on the propyl side chain, or the benzylic positions in the polymer, resulting in a water soluble, complex benzylsulfonic acid. This sulfonation also frees some primary alcohols by virtue of benzyl ether cleavage. This is the site of most of the oxidation during the subsequent exothermic oxidation by dichromate giving the chromium modification (figure 3). The resulting carboxylic, phenolate, and sulfonate anionic functions give good chelating sites for the reduced chromium (III) cation.

The exact nature of the resulting complex is not clearly defined at present; however, it has been definitely shown by McAtee and Smith (ref. 1) that the chromium is firmly chelated such that it may not be removed from the lignosulfonate complex even by strong ion-exchange resins, and that chromium is present in the trivalent oxidation state. Evidence has been given by Jessen and Johnson (ref. 2) and supported in the McAtee and Smith study (ref. 1) that the chrome (III) may also interact with the planar surface of montmorillonite clays by a base-exchange mechanism. This indicates that chromium (III) that is added to a drilling fluid, in the form of a chrome lignosulfonate, is either strongly associated with the lignosulfonate or montmorillonite, such that it does not enter into additional reactions.

TOXICITY STUDIES

Present environmental concerns stress the potential effect that drilling mud chemicals may have if released. Drilling mud thinners are supplied in solid, essentially dust-free form, and therefore spills on land may be removed immediately. Release to an aqueous environment, however, would be difficult to contain because of the product solubility properties. Since these materials are used both on land and offshore, we have tested four commercial products representative of the four classes of drilling mud thinner compounds previously discussed to determine their potential effect on fresh water and sea water fish.



$Cr_2O_7^{-2}$
H
C
SO$_3^-$
OH
O
CH$_3$

Figure 3. Dichromate oxidation of lignosulfonic acid.

Table 1 summarizes the study results. The fresh water and sea water tests were conducted with *Mollienisias latipinna* in accordance with the American Public Health Association Standard Methods (ref. 3). *Mollienisias latipinna* was selected for this study because it has medium sensitivity and can be adapted to fresh and sea water environments. Median Tolerance Limits[*] were established for each thinner after 24, 48, 72, and 96 hours.

This particular study indicates that the tannin class, exemplified by quebracho, has a considerably lower median tolerance limit than any of the other products tested. There was no reason to anticipate this result since high concentrations of tannin compounds are frequently found in natural water systems that flourish with aquatic life. It is suspected that the oxygen scavenging characteristic of this material may have been a factor in this static test procedure. Additional studies have been initiated on the tannin compounds to clarify these results. Sodium acid pyrophosphate shows fairly low median tolerance limits in fresh water, and chrome lignosulfonate and lignite demonstrate the least toxicity in both environments at all time intervals.

In earlier toxicity studies (ref. 4), test materials were separated according to relative toxicity. Substances rated nontoxic killed no test animals, materials designated low-toxicity killed some test animals in concentrations of 500 to 7,500 ppm, and toxic-rated substances killed more test animals at 70 to 450 ppm concentrations. According to these definitions of toxicity, none of the materials tested for this paper fell in the high toxicity category. Phosphate, lignite, and chrome-lignosulfonate all belong in the low-toxicity group.

SUMMARY

The toxicity results presented here are conclusive with regard to the specific test conditions cited and are indicative of the general fish toxicity behavior of these compounds. The median threshold limits

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[*] Median Tolerance Limit (MTL) is the concentration of material tested in which 50 percent of the test animals survive for a specified period of exposure. Thus a high MTL indicates low toxicity, and a low MTL indicates high toxicity.

	Fresh Water				Salt Water			
Thinner	24 hr. TL_m(ppm)	48 hr. TL_m(ppm)	72 hr. TL_m(ppm)	96 hr. TL_m(ppm)	24 hr. TL_m(ppm)	48 hr. TL_m(ppm)	72 hr. TL_m(ppm)	96 hr. TL_m(ppm)
Chrome-Lignosulfonate	7,800	7,800	7,800	7,800	14,200	14,200	12,200	12,200
Quebracho	140	140	140	135	170	158	158	158
Lignite	*	*	35,000	24,500	**	**	**	**
Sodium Acid Pyrophosphate	*	2,000	2,000	1,200	7,400	7,100	7,100	7,100

* There was 100% survival of all test animals at the concentrations tested

** There was 100% survival of all test animals at a concentration of 15000 ppm (This is the practical limit due to the solubility of the chemical tested.)

Table 1. Mollienisias latipinna median tolerance limits for commercial mud thinners in freshwater and seawater.

determined for quebracho, although sufficiently high that it can not be classed as highly toxic, were lower than expected and cannot be explained at present. All the other products tested, including the most widely used drilling mud thinners on the market today, are classed as low-toxicity agents.

The dispersed clay-drilling muds are expected to continue their dominance of the total drilling fluid market. This study suggests that the thinner compounds, which are a vital part of this system, do not offer a serious environmental threat with regard to fish toxicity. Although there is no evidence that any of these materials have been responsible for any environmental damage, it is in the interest of all parties concerned to continue research programs in this area.

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EFFECT OF DRILLING FLUID COMPONENTS MIXTURES ON PLANTS AND SOILS*

R. W. Miller and S. Honarvar†

Abstract

Using undrained, greenhouse pot techniques, 31 drilling fluid (mud) components were tested for their effects in reducing plant growth. Green beans and sweet corn were the test plants; the soil was an excellent, slightly acidic, uncultivated, silt loam soil (Cumulic Haploxeroll). Each component was tested at two addition rates (high and low). The low rates are typical concentrations used in the field. Significant bean yield increases occurred at normal use rates with asbestos, VAMA, and sodium dichromate. No statistically significant reductions of plant yield occurred in soil at normal use rates with asphalt, barite, bentonite, calcium lignosulfonate, sodium polyacrylate, a modified tannin (Desco), a nonfermenting starch, ethoxylated nonyl phenol (DME), a filming amine, gilsonite, a Xanthan gum, paraformaldehyde, pipe dope, hydrolyzed polyacrylamide, sodium acid pyrophosphate, sodium carboxymethyl cellulose, sodium hydroxide, a sulfonated tall oil, and a sulfated triglyceride (Torq-Trim).

A statistically significant (5 percent level) reduction in yield in soil at normal use concentrations occurred with diesel oil, large alcohol, guar gum, a plant-synthetic fiber mix (Kwik-Seal), lignite, potassium, chloride, pregelatinized starch, a modified asphalt (Soltex), and an iron chromelignosulfonate.

When individual components were mixed at normal rates in an equal volume mixture of soil and liquid mud, slight growth reductions occurred with sodium dichromate and the plant fiber mix. Severe growth reductions

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occurred with sodium hydroxide. Higher application rates had greater reduction of plant growth. However, these rates are not typical of normal use.

Reclamation procedures, although not attempted yet, would seem to be relatively simple, with the exception perhaps of the problem with diesel oil, and they involve leaching, additions of gypsum, and time.

INTRODUCTION

Oil well drillers employ a drilling fluid (drilling mud) to carry drilling rock wastes out of the bore hole. This mud is composed of barite ($BaSO_4$), a small amount of bentonite, and various chemicals which produce in the mud certain desirable properties. Some of these properties are an increased carrying capacity, control of fluid loss, stabilizer of unstable shale layers, torque reducer, and water viscosifier. A wide variety of materials are used in the mud for these purposes.

The recent environmental awareness in the United States has prompted well drillers to consider problems of revegetation on the aftermath of drilling. The variety of fluid components used, the climatic variations, soil differences, and desired plant species at various drilling sites increase the amount of information needed in order to make accurate conclusions.

This study is a first look at drilling fluid components which might hinder to some extent the growth of plants. Reclamation activities have not yet been attempted in the research.

REVIEW OF LITERATURE

No available paper in English describing research on the toxicities to plants of drilling mud components was found. Therefore, information on individual components was sought using a different approach.

The following categorization of the 31 components used in this study was used as a guide to the review of literature.

1. Materials that might produce soluble salt effects
   Barite, potassium chloride, sodium acid pyrophosphate, sodium dichromate, and sodium hydroxide.
2. Materials of petroleum origin
   Asphalt, diesel oil, pipe dope, modified asphalt
3. Minerals, coal, or related natural solid deposits
   Asbestos, barite, gilsonite, and lignite.
4. Organics of plant origin other than petroleum or coal-like materials
   Modified tannin, nonfermenting starch, guar gum, Xanthan gum, iron chromelignosulfonate, plant-synthetic fiber mix, calcium lignosulfonate, pregelatinized starch, and sulfonated tall oil.
5. Synthetic and miscellaneous organic materials
   VAMA, sodium polyacrylate, modified tannin, nonfermenting starch, ethoxylated nonyl phenol, large alcohol, filming amine, plant synthetic fiber mix, paraformaldehyde, hydrolyzed polyacrylamide, sodium carboxymethyl cellulose, and a sulfated triglyceride.

Berstein (ref. 3) listed the tolerance to salt of garden (sweet) corn and green beans as given in table 1.

Table 1. Tolerance to salt of corn and green beans

Conductivity (μmhos/cm) at which plant yield will be reduced:	Green beans	Sweet corn
	μmhos/cm	μmhos/cm
10 percent	1.4	2.5
25 percent	2.0	4.0
50 percent	3.0	6.0
100 percent (plant death)	5.0	8.0

Of the materials considered as potential salt problems, barite is too insoluble to be a hazard. The other four materials are all soluble enough to cause a salt hazard if they are added in large enough amounts. The sodium hydroxide will react in soil to form insoluble metal hydroxides or form water with acids; the sodium will adsorb to clays and organic matter in some part. The large amounts of potassium chloride used should cause problems in plant growth as a result of soluble salt concentration.

Of the remaining 27 materials, insufficient literature was available to suggest the presence of materials toxic to plants. The most prominent hazard, diesel oil, has been long used as a herbicide or a carrier for herbicides. Baker (ref. 2) indicates that diesel oil contains materials of carbon chain lengths about C_{14} to C_{18} (boiling range about 250° to 350° C).

The precise action of oils on growth is mostly speculation. The oil is known to penetrate cells and plant organs in general. Some scientists have speculated that the oil penetrates the "oil-miscible" cell membranes eventually destroying their semipermeable nature (refs. 8,14,16). In contrast, the asphalt-like residues seem not to be toxic to plants and, in fact, to be beneficial to plants to some extent, although the beneficial effects are usually not great (refs. 7,12).

Black walnut plants have a phytotoxin called juglone (a 5-OH-1, 4-naphthoquinone) (refs. 4,10). Davis (ref. 4) reported juglone in all parts of the plant. This could be a problem substance in the plant synthetic fiber mix.

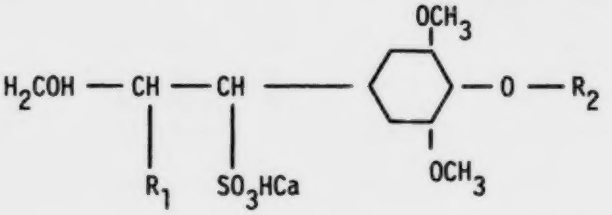
The lignosulfonates are large, organic molecules containing many aromatic units. Upon hydrolysis (decomposition), intermediate breakdown products might be toxic. Decomposition of tannins might produce phytotoxins by a similar process.

Chromium (Cr) is a potential toxin. The normal soil content is near 100 parts per million (ppm); this study will be adding in the high but unusual rates up to nearly 4,000 ppm Cr (ref. 5). At levels of 1,370 to 2,740 ppm Cr citrus had chlorosis (ref. 15). In greenhouse studies, oats were stunted, and had narrow, reddish-brown leaves with necrotic (drying) areas (ref. 15).

EXPERIMENTAL MATERIALS AND PROCEDURES

The materials studied and their rates are given in table 2. A brief list and discussion of each material is given in the following list.

1. Asbestos or Super Visbestos^{R} (chrysotile). Asbestos, a natural mineral, is used to increase carrying capacity, flow properties, and stabilize gelation of bentonite. The chemical compositon ($H_4Mg_3Si_2O_9$) suggests that asbestos should not adversely affect plant growth.
2. Asphalt (blown). Asphalt is used as a differential sticking agent, shale stabilizer, torque reducer, and fluid loss control agent. Prepared by air oxidation of petroleum residium, asphalt is composed of hydrocarbons (saturates, naphtheme aromatics, polar aromatics, and asphaltene) of molecular weights from 600 to over 4,000.
3. VAMA or Ben-Ex^{R}. VAMA is used as a bentonite extender and selective flocculent to remove cuttings from the cycled mud. Originally marketed as a soil conditioner, VAMA is a copolymer of vinyl acetate and maleic anhydride.
4. Calcium Lignosulfonate. This material is used primarily to aid dispersion of clays. Caclium lignosulfonate is a substituted phenolpropane:



   The R_1 and R_2 may be additional phenolpropane molecules.

5. Sodium Polyacrylate (Cypan^{R}). Sodium polyacrylate is used to control fluid loss by forming a clay-polymer network at the bore wall. It is a polymer of acrylonitrile made to the desired molecular weight. It resists microbial attack.

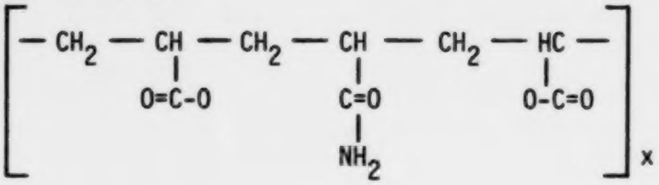


Table 2. Drilling mud components and their concentrations added to soil for observing effects of components on plant growth. Rates are given in pounds per barrel (lb/bbl) and in grams per 1.6 liters of soil. For the test soil, 1.8 kg of soil equalled about 1.6 liters.

Mud Component	Levels tested	
	lb/bbl of soil (proposed)	g/1.8 kg of soil (actually used)
Asbestos (Super Visbestos^{R})	2 and 5	8.18 and 20.5
Asphalt (blown)	1 and 5	4.09 and 20.5
Vinyl acetate polymer (Ben-Ex^{R})	0.05 and 0.2	0.21 and 0.82
Calcium lignosulfonate	3 and 20	12.28 and 81.9
Sodium polyacrylate (Cypan^{R})	0.5 and 1.5	2.05 and 6.14
Modified tannin (Desco^{R})	0.25 and 3	1.02 and 12.3
Non fermenting starch (Dextrid^{R})	1 and 10	4.09 and 40.9
Ethoxylated nonyl phenol (DME^{R})	0.5 and 3	2.05 and 12.27
Diesel oil	1[a] and 10[a]	18 and 180
Large weight alcohol (Drillaid 405^{R})	0.2 and 1	0.82 and 4.09
Filming amine (Drillaid 412^{R})	0.1 and 0.3	0.41 and 1.23
Gilsonite (a fossil resin)(Super Lube Flow^{R})	1 and 5	4.09 and 20.5
Guar gum (Gendril Thik^{R})	1 and 6	4.09 and 24.5
Xanthan gum (Kelzan-XC^{R})	0.5 and 2	2.05 and 8.18
Plant-synthetic fiber mix (Kwik-Seal^{R})	5 and 50	20.5 and 182[b]
Lignite (Ligco^{R})	2 and 10	8.18 and 40.9
Paraformaldehyde	0.1 and 0.3	0.41 and 1.23
Pipe dope	0.1 and 0.3	0.41 and 1.23
Potassium chloride	10 and 30	40.9 and 122.7
Pregelatinized starch (corn starch)	1 and 10	4.09 and 40.9
Iron chromelignosulfonate (Q-Broxin^{R})	3 and 20	12.28 and 81.9
Hydrolyzed polyacrylamide (Separan AP-273^{R})	0.5 and 2	2.05 and 8.18
Sodium acid pyrophosphate	0.1 and 0.5	0.41 and 2.05
Sodium carboxymethyl cellulose	0.5 and 1.5	2.04 and 6.14
Sodium dichromate	0.5 and 3	2.05 and 12.3
Sodium hydroxide	1 and 5	4.09 and 20.5
Modified asphalt (Soltex^{R})	0.5 and 2	2.05 and 8.18
Sulfonated tall oil (Witconnate 1840^{R})	0.5 and 3	2.05 and 12.3
Sulfated triglyceride (Torq-Trim^{R})	0.5 and 1.5	2.05 and 6.14
Barite	100 and 350	364[c] and 955[c]
Bentonite	7 and 35	28.6 and 135[d]

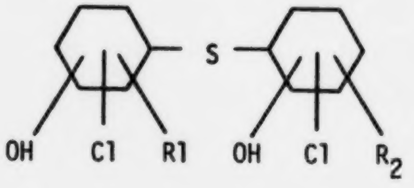
[a] Percentage by weight.

[b] 182 g/1.6 kg of soil.

[c] 364 g/1.6 kg of soil and 955 g/1.2 kg of soil.

[d] 135 g/1.7 kg of soil.

6. Modified Tannin (Desco^R). The only data available is from J. L. Lummus (Amoco Products Co.) describing Desco as a "modified tannin neutralized with an alkaki." Tannins are large, complex molecules containing ring alcohols, large ring acids, and many less well-known organics.
7. Nonfermenting Starch (Dextrid^R). Dextrid is an adsorptive colloid designed to limit the rate of hydration of shale formations and serve as a filtration control agent for permeable formations. Its composition is described in U.S. Patent 3,256,115. It is a microbially stable, gelatinized, starchy flour with from 1 to 5 percent paraformaldyhyde and 1 to 5 percent of a compound with the following structural formula:



Where R_1 and R_2
are selected
chloride (Cl)
and H

8. Ethoxylated Nonyl Phenol (DME^R). DME is an oil-in-water emulsifier.
9. Diesel Oil. Common diesel oil is an intermediate molecular weight petroleum distillate. Used number 2 diesel oil.
10. Large Weight Alcohol (Drillaid 405^R). Drillaid 405, a diesel oil replacement, is a private formula and is unavailable to the writer. It is said to be biodegradable and a nonpollutant. It reduces torque, drag, and differential pressure, and aids in hole stability.
11. Filming-Amine, Inhibitor (Drillaid 412^R). Drillaid 412 is an oil-soluble, water dispersable, organic, filming-amine inhibitor used to retard hydrogen sulfide and oxygen corrosion of drill pipe. This material's composition is a private formula and unavailable, but contains amine salts. The material is used as a coating on drill pipe rather than by treating the drilling mud.
12. Gilsonite (Super Lube Flow^R). Gilsonite is used for mechanical stabilization, chemical inhibition, and surface hydration. It is "one of the natural fossil resins." According to the information from

the supplier, it is listed in "Foods and Drugs" as being safe in food-contact surfaces.

13. Guar Gum (Gendril Thik^{R}). Guar gum is used as a water viscosifier. It is ground endosperms of *Cyamopsis tetragonolobus* (a legume called Guar or cluster bean). The molecule is a straight-chain mannan having single branches of galactose. Its average molecular weight is 22,000.

14. Xanthan Gum (Kelzan-XC^{R}). Kelzan is used as a viscosifier in drilling fluids. It is a xanthan gum produced by fermentation of a carbohydrate by the bacteria *Xanthanomas campestis*.

15. Plant-Synthetic Fiber Mix (Kwik-Seal^{R}). A material added to seal porous geologic formations. Kwik-Seal is a blend of ground walnut shell, two vegetable fibers, two synthetic fibers, and cellophane.

16. Lignite (Ligco^{R}). Lignite is used to emulsify oils in water-based drilling fluids and to control filtration rates of these fluids. Ligco is a ground lignite which is a low rank of coal classified between peat and subbituminous coal.

17. Paraformaldehyde. Paraformaldehyde is used as a preservative in conjunction with starch. It is a polymer represented by $(CH_2O)_x$.

18 Pipe Dope. Pipe dope is a partially refined petroleum oil thickened with a calcium soap of abietic acid with 10 percent red lead oxide dispersed in it.

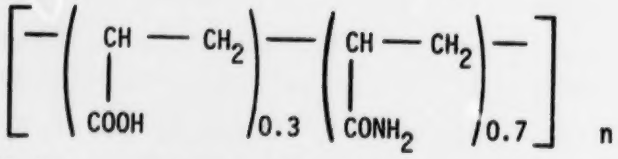
19. Potassium chloride (KCl). Potassium chloride is used in combination with other chemicals, such as Separan AP-273. It helps stabilize sensitive shale formations encountered while drilling.

20. Pregelatinized Starch. This starch is an amylose carbohydrate (sugar units) with 7.5 percent protein.

21. Iron Chromelignosulfonate (Q-Broxin^{R}). Q-Broxin is used primarily as a thinner or dispersant to lower the apparent viscosity and gel strength of mud. Caustic soda is usually also used giving a mud of pH 9 to 10. Additional composition is given in U.S. Patent 2,935,504.

22. Hydrolyzed Polyacrylamide (Separan AP-273^{R}). At low concentrations, 25-50 ppm (about 0.008-0.018 lb/bbl), Separan is a flocculant for maintaining a low-solids content. At rates of 1,000 or 3,000 ppm

(0.3 to 1.0 lb/bbl) in combination with 3 to 15 percent KCl, Separan stabilizes water-sensitive shale formations encountered while drilling. It has a molecular weight of 3 x 10^6 or greater and a formula as follows:



$$\left[-\left(\underset{\substack{| \\ \text{COOH}}}{\text{CH}} - \text{CH}_2 \right)_{0.3} - \left(\underset{\substack{| \\ \text{CONH}_2}}{\text{CH}} - \text{CH}_2 \right)_{0.7} - \right]_n$$

Separan AP-273 is a partially hydrolyzed polyacrylamide and is similar to hydrolyzed polyacrylonitriles (HPAN), differing mostly in extent of hydrolization. HPAN has been used to form stable soil structure. It is manufactured by Dow Chemical Company and supplied by the Shell Development Company.

23. Sodium Acid Pyrophosphate (SAPP). SAPP is used as a reducer of viscosity. Its composition, $Na_2H_2P_2O_7$, does not indicate any reason for damaging action on plant growth.

24. Sodium Carboxymethyl Cellulose (SCMC). SCMC is used to reduce fluid loss. It is composed of 70 to 99 percent sodium carboxymethyl cellulose, and its formula is $R\text{-}O\text{-}CH_2COONa$, where R=glucose units in chains.

25. Sodium Dichromate. The reason for employing sodium dichromate is not yet known, but is presumed to be for making the salt of lignosulfonates which help increase clay dispersion. Its chemical composition is $Na_2Cr_2O_7$.

26. Sodium Hydroxide. Sodium hydroxide, NaOH, is a strong base. It is a well-known soil dispersant and aids in the breakdown of soil aggregates. It is often used in drilling muds with calcium lignosulfonate, lignite and Q-Broxin, resulting in a mud of pH 9 to 10.

27. Modified Asphalt (SOLTEX^R). Soltex is a modified, high-molecular-weight hydrocarbon, possibly a sulfonated asphalt.

28. Sulfonated Tall Oil (Witconnate 1840^R). Witconnate 1840 is a mixture of resin acids (35-40 percent) and fatty acids (50-60 percent) from acid treatment of pine wood.

29. Sulfated Triglyceride (Torq-Trim^R). Torq-Trim is used to improve lubricity. It is a sulfated triglyceride containing aliphatic and short-chain alcohols.

Greenhouse Procedure

The soil used is the Dagor silt loam series, a dark-colored soil under "scrubby maple". In the U.S. Soil Classification system, Dagor silt loam is a Cumulic Haploxeroll, fine-loamy, mixed, mesic. It has a deep A1 horizon, 0 to 34 inches. Its general properties are given in table 3.

The study was done in two parts. Part A had individual mud components added only to soil. Part B, done later only on materials causing reduced plant growth, had individual mud components added to the liquid mud, which was then added to an equal volume of the soil. The mixture was dried, crushed, mixed, and planted. The soil-mud volume of Part B was equal to the soil volume of Part A and contained the same weights of components per 1.6 liter. Pots had no drainage but were watered by adding water until the pot was a predetermined weight. Weight of plant growth was estimated to allow increased pot weight with plant size. Fertilizer nitrogen and phosphorous was added to eliminate these nutrients as growth restrictions.

Because of timing in arrival of fluid components, several dates of planting were involved. Each planting had its own set of controls. In most plantings (except Part B-corn), natural light was the only light source.

The mud base used was: 294 cm^3 of water plus 13 g of bentonite, mix well; after overnight, add 194 g of barite. Plants used were green beans and sweet corn.

Analytical Tests

Soluble salts were determined by electrical conductivity of the saturation past extract (ref. 6).

Soil pH on treatment and control samples was measured on a 0.01 Molar $CaCl_2$:soil suspension which results in pH values about 0.5 pH unit lower

Table 3. Characteristics of Dagor silt loam

Item	Value
Clay	10%
Oxidizable organic matter content	8.1%
Soil pH, paste	6.2%
Soil pH, 1:2 soil:0.01 M. $CaCl_2$	6.0
Cation exchange capacity	34.3 me/100g
Field capacity (1/3 bar suction)	34.7%
Wilting percentage (15 bar suction)	16.8%
Available phosphorus	130 kg/ha (high)
Available potassium	1,150 kg/ha (high)

than paste pH values (ref. 13). Soil characterization pH values were done on a soil paste, a standard procedure (ref. 13).

Moisture retentions values for one-third bar and 15 bars of moisture suction were obtained on pressure plates using standard procedures (done by the Utah State Soil Testing Laboratory).

Organic matter was measured by the Walkley-Black method of wet oxidation with potassium dichromate and sulfuric acid and back titration with ferrous sulfate (ref. 1).

Cation exchange capacity values were done by the Utah State University Soil Testing Laboratory using the Standard ammonium acetate extraction and measurement of the replaced ammonium ion. Exchangeable K was measured on this extract.

Available P was done by the sodium bicarbonate extraction procedure of Olsen and Dean (ref. 12).

Chromium was analyzed using an atomic absorption spectrophotometer after extraction of chromium by wet digestion of plant material with nitric-perchloric acid or with 1:10 soil to 2 N KCl extraction of chromium from soils.

RESULTS

Evaluation of the effects of added mud components on plant growth was a combination of visual observations, photographic records, and yield values. Dry weight values are given in tables 4 and 5 for Part A (components added to soil only). The "low rates" are the typical (normal) concentrations that would result if the components were in muds and then added to and mixed with an equal valume of soil. Three materials at the normal rates increased bean growth, five caused a slight but statistically significant reduction, and six caused even greater growth reductions.

The materials which caused reduced plant growth in soil alone were then added to the drilling mud base and this mixture added to an equal volume of soil, then dried, mixed, and planted. Yields are shown in table 6.

Table 4. Oven-dry yield weights, in grams per pot, of green beans and sweet corn grown on Dagor silt loam with individual mud component added. Each value is an average of two replication; the control value an average of 9 for beans and 10 for corn (late planting).

Material	Beans		Corn	
	Low rate	High rate	Low rate	High rate
Nonfermenting starch	23.5	7.0[a]	28.5	2.0[a]
Ethoxylated nonyl phenol	18.0	23.5	38.0	35.0
Pipe Dope	21.5	20.0	34.5	19.5[a]
Iron chromelignosulfonate	17.0	6.0[a]	26.0[a]	6.0[a]
Sulfonated tall oil	21.5	16.0	31.0	23.5[a]
Sulfated triglyceride	19.5	10.0[a]	25.5[a]	11.0[a]
Control (soil only)	21.1		36.9	
LSD (Controls vs. treatments at 95%)	6.05		7.78	
LSD (Controls vs. treatments at 99%)	8.25		10.59	

[a] Highly significant yield decrease (99% confidence level).

[b] Statistically significant yield decrease (96% confidence level).

Table 5. Oven-dry yield weights, in grams, per pot, of green beans and sweet corn grown on Dagor silt loam with individual mud component added. Each value an average of two replications; the control value an average of 20 replications (early planting).

Material (component)	Beans		Corn	
	Low rate	High rate	Low rate	High rate
Asbestos	29.5[a]	25.0	45.0	45.0
Asphalt	27.0	27.0	45.0	42.0
Barite	25.0	24.5	46.5	38.0[b]
VAMA	29.5	30.0	48.5	50.5
Bentonite	27.0	23.0	41.5	40.5
Calcium lignosulfonate	26.5	10.0[c]	47.5	13.0[c]
Sodium polyacrylate	25.0	26.5	46.0	46.0
Modified tannin	28.0	22.5	41.0	33.5[c]
Diesel oil	13.0[b]	3.0[c]	14.5[c]	1.0[c]
Large weight alcohol	21.5[b]	22.5	44.0	17.5
Filming amine	25.5	26.0	40.0	39.5[b]
Gilsonite	27.5	29.0	42.0	46.0
Guar gum	9.0[c]	6.5[c]	42.0	2.0[c]
Xanthan gum	27.5	25.0	47.0	34.5[c]
Plant-synthetic fibers mix	16.5[b]	10.5[b]	26.0[c]	2.0[c]
Lignite	21.5	24.5	48.0	45.0
Paraformaldehyde	28.0	24.5	46.5	50.5
Potassium chloride	3.0[c]	0	5.5[c]	0.5[c]
Pregelatinized starch	20.5[b]	16.0[b]	38.5[b]	2.0
Hydrolyzed polyacrylamide	27.5	23.0	48.5	46.0
Sodium acid pyrophosphate	26.0	27.0	48.5	45.5
Sodium carboxymethyl cellulose	22.5	29.0	45.5	45.5
Sodium dichromate	20.5[a]	2.5[c]	40.0	2.0[c]
Sodium hydroxide	25.5	4.0[c]	46.5	21.0[c]
Modified asphalt	24.5	29.0	38.5[b]	36.5[c]
Controls (soil only)	25.6		47.3	
LSD (controls vs treatments at 95%)	3.89		7.66	
LSD (controls vs treatments at 99%)	5.18		10.17	

a Statistically significant yield increase (95% confidence level).
b Statistically significant yield decrease (95% confidence level).
c Highly significant yield decrease (99% confidence level).

DISCUSSION OF RESULTS

Three factors should be kept in mind as the results of this study are considered. First, the "low rate" is the normal concentration used in field work; second, no leaching of the soil was permitted; and third, no ameliorating chemicals were added.

Although many of the materials tested in soil in Part A caused some growth reduction, when mixed one volume of soil to one volume of mud the results were somewhat different. The modified tannin (Desco) actually increased bean growth at normal use rates (low rate). Also, no effects on growth were observed at normal used levels from additions of nonfermenting starch (Dextrid), modified tannin (Desco), the large weight alcohol (Drill-aid 405), guar gum, pregelatinized starch, and the sulfated triglyceride (Torq-Trim) (see table 6); growth reductions had occurred in soil only.

The materials which caused plant growth reductions in the soil-mud mixture may not cause similar problems in the field because of a number of restrictions inherent in the greenhouse procedure. These restrictions and limitations need to be considered.

The absence of drainage, which would be expected to occur in the field, eliminates leaching of any soluble toxic materials. Soluble salts--potassium chloride, sodium dichromate, and sodium hydroxide--are readily removed in large part by small amounts of leaching water. Leaching plus the addition of gypsum or sulfur will help replace adsorbed sodium and remove it from the profile, thus eliminating some or all of the problem due to sodium hydroxide.

The majority of known organic materials listed in the literature as phytotoxins and which seem possible to be released from the studied components are water-soluble substances. These organic compounds should move with water leaching down below the soil profile. Even without leaching, these phytotoxic compounds should decompose quite rapidly (within a year) and, at the worst, be temporary problems to plant growth.

Also, keep in mind the conditions of the tests: Warm temperatures and rapid, intense growth; soil-mud mixtures of about equal volumes of

Table 6. Oven-dry yield weights, in grams per pot, of green beans and sweet corn grown in Dagor silt loam and the base mud mixture with the individual mud component added. Each value an average of two replications; the soil control values an average of 12 for beans 11 for corn; and soil-mud control values an average of 11 for beans, 12 for corn.

Material	Beans		Corn	
	Low rate	High rate	Low rate	High rate
Calcium lignosulfonate	9.8^{a}	$0^{b\,a}$	5.7^{b}	$0^{b\,a}$
Nonfermenting starch	13.3	6.7^{b}	14.2	2.2^{b}
Modified tannin	15.0^{c}	7.8^{b}	14.1	8.5^{a}
Diesel oil	6.3^{b}	1.4^{b}	3.6^{b}	0^{b}
Large weight alcohol	12.0	12.7	11.8	11.2
Guar gum	12.4	1.2^{b}	13.0	1.1^{b}
Plant-synthetic fibers mix	10.7	6.5^{b}	9.3^{a}	0.3^{b}
Lignite	9.2	0^{b}	2.9^{b}	0^{b}
Potassium chloride	0^{b}	0^{b}	0^{b}	0^{b}
Pregelatinized starch	9.9	5.9^{b}	13.6	3.9^{b}
Iron chromelignosulfonate	10.0^{a}	3.7^{b}	11.4	3.8^{b}
Sodium dichromate	8.9^{b}	0^{b}	^{b}	0^{b}
Sulfated triglyceride	10.4	9.1	14.5	11.2
Controls, soil + mud	12.2		12.8	
Controls, soil only	10.7		10.1	
LSD (soil control vs treatments, 95%)	2.41		3.52	
LSD (soil control vs treatments, 99%)	3.23		4.69	

[a] Statistically significant yield decrease (95% confidence level).
[b] Highly significant yield decrease (99% confidence level).
[c] Statistically significant yield increase (95% confidence level).

soil and liquid mud; and a MAXIMUM "accident" rate of addition as well as the lower, normal use rate. Variations in these factors will cause changes in plant responses. Also, beans are considered relatively sensitive to salt and many toxins. Many native plants at drilling sites may be quite tolerant.

With these cautions emphasized, the data of table 7 summarize much of this preliminary phase. Only six of the final 13 components at normal use concentrations reduced plant growth. But only four materials seem to be of real concern.

Potassium chloride is used in concentrations too high to permit plant growth in the residual mud. However, the salt is very soluble, and potassium is a plant nutrient. Often potassium is in deficient amounts in rainfall areas exceeding about 30 inches (75 cm) annually. In such regions, leaching would remove excess salts and the adsorbed portion of potassium could be beneficial to plant growth.

Table 7. Summation of the effects of 31 drilling fluid (mud) components in reducing bean and corn growth when normal-use rates are added and the liquid mud is added to an equal volume of soil

Material	Dry yield, percent of control	
	Beans	Corn
Nonfermenting starch (Dextrid^{R})	109	111
Modified tannin (Desco^{R})	123[a]	110
Guar gum	102	102
Large weight alcohol (Drillaid 405^{R})	98	92
Sulfated triglyceride (Torq-Trim^{R})	85	113
Pregelatinized starch	81	106
Iron chromelignosulfonate (Q-Broxin)	82	89
Plant-synthetic fiber mix (Kwik-Seal)	88	73
Calcium lignosulfonate + NaOH	80[b]	45[b]
Lignite (Ligco^{R}) + NaOH	75[b]	23[b]
Diesel oil	52[b]	28[b]
Sodium dichromate	73[b]	0[b]
Potassium chloride	0[b]	0[b]

[a] Statistically significant increase in yield.

[b] About 20 and 27 percent statistically significant reductions for beans and corn, respectively.

The second and third most toxic components of the drilling muds tested were lignite and calcium lignosulfonate, but only because of the sodium hydroxide levels added with them. The high soil pH and soil dispersion resulting from adsorbed exchangeable sodium are the problems common to SODIC soils, which are well known to agriculturalists. The accepted treatments for such soils are the addition of gypsum ($CaSO_4 \cdot 2H_2O$) or sulfur (elemental) followed by leaching. These treatments should solve this problem.

The fourth most toxic material, diesel oil, may be the most difficult problem to solve. Fortunately, alternatives to its use are already available and appear to be nontoxic (see Drillaid 405 of this paper). The distillates in diesel oil will eventually vaporize into the atmosphere leaving limited or no phytotoxic materials. Some of its high-boiling-point compounds may remain adsorbed to soil tending to "water-proof" the soil to some extent. In areas of low yearly moisture, the intentional water-proofing of soil--if the soil is also porous--has helped increase total usable water. The long range effects of diesel oil should not exceed a year.

The influence of sodium dichromate is unclear. It is known from other analyses in this study to be at least partly a soluble salt effect in the unbuffered barite making up the bulk of the mud. This salt effect is easily removed by leaching. The possibility of chromium toxicity exists--addition rates are high enough--but experimental verification is lacking.

Some of the remaining components decreased plant growth. Except perhaps for toxins in black walnut shells, the plant-synthetic fibers mix (Kwik-Seal), the tannin (Desco), and the iron chromelignosulfonate (Q-Broxin), no other toxins were anticipated. The effects of the gums and starches particularly were surprises. It is presumed that any phytotoxins present are likely to be short lived and mostly water soluble. A combination of leaching and a few months of warm weather should largely eliminate any toxins present. Work on these aspects of amelioration are in progress on a limited scale.

The writer does not believe the drilling fluid components tested, except perhaps diesel oil, pose severe problems to growing plants. At least three simple processes can reduce any phytotoxicity of most of the tested materials. First, leaching can remove salt and soluble organics. Second, soil burial can provide an adequate root zone above the mud. Third, gypsum or sulfur can be added to correct the high alkalinity and exchangeable sodium problem of added sodium hydroxide.

More careful studies of the soil chemistry of chromium and the longevity of diesel oil effects are needed. These studies could clarify the environmental effects of these mud components.

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DISCUSSION

CHAIRMAN LUMMUS: The gentlemen who have just presented their papers on the effect of mud additives in the environment are ready to answer questions.

DR. PAT M. WENNEKENS (Alaska Department of Fish and Game, Anchorage, Alaska): I think the results presented are quite interesting, but I also think they can be very misleading. One consideration is that in order to perform appropriate tests, we try to select the toughest animal available, because it can be kept alive during laboratory handling in preparation for the tests. This is in many instances a very misleading approach, because we like to determine what is the effect on the most sensitive portion of the biological system, not the toughest portion of the system.

The second, concerning the last presentation, is that unless we look at the total mass balance of where all this material goes and what it does when it goes in different places, we don't get a perfect picture. As an example, by adding gypsum and leaching we can improve the soil, but the leachate also goes someplace. This is the area in which we are also very much concerned; any material being used or spread on the land as a byproduct also goes someplace and does certain things. And I think unless we make some kind of presentation and look at what the total mass balance of all of the components of the system do, we have a very misleading picture.

MR. REED E. HARRIS (National Marine Fisheries Service, Anchorage, Alaska): It is all well and good that we have studied these things individually. I wanted to know if, in fact, there have been studies conducted that deal with drill muds as a whole, in other words, whether or not we have synergistic effects on all of these different additives in drilling muds, and what effects they might have.

I would also like to ask why the subject mollienisia was selected as a test animal rather than some other organism?

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CHAIRMAN LUMMUS: I can answer the first question.

The effect of muds and the possible synergistic effect of typical muds, which would contain a combination of additives, will be studied in the next phase, phase two. In that phase we are going to involve not only the effects of the combination of additives but also the effects of reclamation procedures.

MR. HOLLINGSWORTH: I would like to address myself to the other part of your question dealing with the selection of *M. latipinna* as a test organism. I think we stated in the paper that the test organism *M. latipinna* is described as being a median sensitivity approach and is adaptable both to freshwater and seawater environments. Thus it makes it an ideal organism for some initial screening work. And we are cognizant that the reactions of this particular species are not necessarily indicative of all other organisms' responses to these materials, but it is a satisfactory organism for doing our initial screening work.

MR. REED E. HARRIS: Do you plan on doing work on synergisms in fresh water? Do you plan on doing any work on freshwater species as well as saltwater species?

MR. HOLLINGSWORTH: Yes. I am sure we will get into that, eventually.

MR. KEITH E. JAMES (Texian International, Houston, Texas): I will try to avoid making a complete speech here. We, among other things, run many bioassay tests. The sail-fin Mollie, *M. latipinna* has been mentioned here as one of these fish. Since this question has come up from time to time, I might make some comments on it.

We have correlated this with several other fish, a couple of species of ocean minnows, three species of shrimp, a couple of species of plankton. Naturally, we do not compare plankton with shrimp or with fish; we are talking about different digestive systems and different metabolisms. The gentleman raised a relevant question, but I would suggest you keep in mind that we are talking about acute toxicity rather than long-term effects. Obviously, if we kill the fish's food supply, even though it lives 96 hours, it is going to have a rough time thereafter. So, let us not confuse the two different types of tests.

The sail fin mollie, which we compared with several fish, is obviously convenient, for one thing. It will grow in both freshwater and saltwater, with gradual conditioning. It is also a sensitive fish. If we use gar or goldfish, everything would look pretty good. Some say trout will look terrible; but not necessarily. We have correlated with trout in a few cases, not in our lab but between other labs on some of the same products, and the sail fin Mollie does not look much more (or less) stable than trout, actually. But I do not think it is accidental that the "powers-that-be" running LD_{50}'s and TL_M's for many years, rarely specify particular organisms. As long as we know the organism is comparable in some way, I think this tells us what we want to know. There have been a lot of lists made of common fish. If there is a list of only those that are acceptable, I would like to hear about it, but there are only some lists of suggested fish. But I do not think we should try to key in too heavily on one particular specie unless we can think of some reason to eliminate it.

MR. DOYLE D. WALLER (IMCO Service, Houston, Texas): Regarding the question asked earlier by the gentleman from the University of Texas on turbidity, I want to make this comment.

The Department of Interior, Bureau of Land Management, has a bulletin, Environmental Impact, 74-90, which would answer it very well. Based on 25 years of cuttings and miscellaneous mud spills in the Gulf of Mexico, turbidity has not proven to be any problem, to date; neither have settlements on the bottom. The fish, plankton, as well as game fish, have multiplied steadily. This is documented in that particular statement. I would suggest that the people who have not read that do so.

DR. GEORGE H. HOLLIDAY (Shell Oil Company, Houston, Texas): I understood that Dr. Rice at the Marine Fishery Service at Auke Bay had made an offer to do some testing of hole muds, and that that particular offer had been rejected--I am not sure whether it was by EPA or by the

National Marine Fishery Service. I wonder if Mr. Harris would like to talk a little bit about the proposal that was made and perhaps the history behind it?

MR. REED E. HARRIS: All this work is preliminary; we were trying to get funds or get a study funded by the various participants in the drilling operations in Cook inlet. And Mr. Rice has accepted, or I think would be amenable to accepting a study if it were funded by the various companies that are involved in oil exploration.

As we talk about this, we are now in the process of talking to some of the oil companies, including Phillips, Shell, and some of the other operators to conduct studies that relate to the possible effects of muds and their additives on marine life. I think Mr. Rice, at the Auke Bay lab, National Marine Fishery Service Lab, would be amenable to do those studies if they are funded.

We would also like to contract out an in situ study on some of the effects of muds "in place" on the bottom. This way we will not be dealing with individual components in drilling muds; we will be dealing with the real fact.

I do not know if any of you are aware that in Alaska we have not patently accepted this idea that drill muds are harmless. And there have been cases where we have asked that the drilling muds and cuttings be hauled ashore until we can find out. So, basically, that is what we are after right now; we are trying to find out so that the companies do not feel like we are leaning on them.

I believe that once we can undertake a study, and we can show one way or the other whether or not in real life there is an impact upon the marine environment or the marine biota, then we will modify our stipulations on our Corps of Engineers permits.

But I believe Mr. Rice would be willing to accept the oil industry's money if they are willing to find out what the impact will be.

I am not aware that he has refused any study of that sort. In fact, he is doing work for Shell Oil right now on the toxicity of Cook inlet crude.

DR. RICHARD S. SCALAN (University of Texas, Marine Science Institute, Port Aransas, Texas): I have a comment regarding the subject of the environmental impact statements and the effects of long-term drilling in the ocean. One thing we do not have, and for which the Bureau of Land Management is now funding quite a large amount, is a baseline study to know whether or not there has been an effect on the environment. We are engaged in such a study in South Texas waters; such studies will go on in the East Coast, the West Coast, and in Alaska. These studies are designed to find out what now exists so that we will be able to make some statements about whether or not the environment has been affected by such things as drilling muds or the drilling activities themselves.

Now, as far as the turbidity is concerned, as I mentioned awhile ago, I am a chemist, but the biologists tell me that the one thing that they will be able to see beyond any doubt is that you can measure and correlate the turbidity of the waters with the organisms, the microorganisms, primarily with phytoplankton, after the phytoplankton come zooplankton and the fish follow them. I don't know whether it is good, bad, or indifferent to force the phytoplankton to a higher level where they can get the sunlight.

My point is, that this is probably the one thing that will be affected, and the one sort of thing that will come out of such studies as these baseline studies that the Bureau of Land Management is now sponsoring.

DR. ROBERT Y. GEORGE (University of North Carolina, Wilmington, N. C.): I would like to make two brief comments with reference to the questions raised. And I would like to address a question to Dr. Miller.

The comments are primarily pertaining to the acute experiments, fish toxicity experiments, which were reported. Obviously, there is a need for chronic or long-term study to follow up. Mere survival does not answer a lot of the questions we need to know about the behavior changes and related alteration in physiological processes concerning the health of the animals in terms of their ability for growth and reproduction.

With reference to the turbidity, of course, the plankton trapped in a plume of mud cannot photosynthesize like the normal algae or diatoms do, but turbidity is not necessarily a long-term phenomenon. And migrating animals have a tendency to escape.

The question I have in mind for Dr. Miller concerns the higher nodulation that is encountered in the beans. Is it seen only in the barite substrate or in other substrates? And are there other factors that induce nodulation?

DR. MILLER: There is no possible way to know this because there was not enough information taken. We only made observations of the pots because we had other things that we were needing to do.

I presume that the nodulation is a combination of two things, at least. The first is that a lack of nitrogen nearly always increases nodulation. A second is that any kind of toxicity hindering bacterial growth might reduce nodulation. So there is no way to know.

It simply appeared that the bean in the barite was much more nodulated than any of the test pots. Lignin, lignite, and calcium lignosulfonate all seemed to be fairly well nodulated in spite of the fact that they are organic substances. So I have no information of value that I can give you on that.

DR. C. S. GIAM (Texas A & M University, College Station, Texas): I think one of the problems that we are having here is the fact that we really have not investigated the effects of various chemicals on biota very carefully. But I would like to point out and remind some of you that in cases where petroleum or copper have been studied, at lower levels they were found to be beneficial to the systems; at higher levels they are toxic.

So when we talk about toxicity, especially when we talk about high and low dosages without actually mentioning the number, we have got to be very careful.

Concerning copper in particular, there are some studies (NSF-IDOE-CEPES) in which copper concentrations used were near or slightly higher than natural (ambient) levels. At certain parts per billion level, copper was reported to increase growth of particular organisms. However, at 10 or a hundredfold beyond this level, there was an inhibition of growth on these organisms.

So, we may be in a controversy over nothing (various concentrations of copper gave different observations).

DR. WENNEKENS: In some of your additives you have a byproduct of hemlock and cedar. Is this hardwood, or does this include the bark? I mean, does it include both the bark and the wood or only hardwood or bark, or what? What kind of material is it? Can you give me any information on this?

CHAIRMAN LUMMUS: I assume, I believe I am correct, that it includes only hardwood? Is that correct?

DR. MILLER: No. It is an extract like your quebracho or hemlock or redwood.

MR. HOLLINGSWORTH: Yes. I think the quebracho extract, for example, comes from the heartwood of the quebracho tree whereas most of the others are bark extracts, water-soluble extracts. I haven't gone over the entire list, but I think that is essentially correct.

DR. WENNEKENS: I asked the question because there are some studies that show that some trace sediments in the woods--and especially in the bark, where they are concentrated--actually are hormone inhibitors. And I question it because some of those woods are known to be very resistant to rot, meaning that they have some biocidal properties, which have components that are essentially biocidal. And there has been some work demonstrating hormone inhibitors to the metamorphosis of larvae.

CHAIRMAN LUMMUS: When you asked the question, I was thinking in some of the slides that we had some wood fibers and plant fibers. Now, these are mostly used in lost circulation materials, because this would be the ground-up wood. We are talking about some of the extracts; they would be from the bark. I hope that clarifies it.

DR. MILLER: The point I want to make is that unless we look at what components are most liable to have some direct effects, again, as I told you, you can put cedar shavings in your closet for mothproofing of your closet, that means you are killing the moths. But some of those components actually can inhibit the larvae to metamorphose, to go from a larva to an adult. And a question that we have is essentially what this does if you release this material in an area where you have a very high shrimp juvenile or shrimp larvae that are being spawned at the present time.

USE OF A BIOASSAY TEST IN EVALUATING THE TOXICITY OF DRILLING FLUID ADDITIVES ON GALVESTON BAY SHRIMP

B. G. Chesser and W. H. McKenzie*

Abstract

The effect of drilling fluids and drilling fluid additives on marine life is obviously an important consideration when drilling in coastal and offshore waters. This paper describes the use of a bioassay test to determine the degree of toxicity of drilling fluid additives to Galveston Bay shrimp. Shrimp were chosen as the test organism since they are not only an important commercial food crop but a biologically important food for fish and other marine organisms.

The method used is patterned after that given in the Standard Methods for the Examination of Water and Wastewater, 13 ed., prepared and published jointly by American Public Health Association, Water Pollution Control Federation, and American Water Works Association. Methods of collecting, acclimatization, and exposure as well as the test apparatus are described. The results of 96-hour salt water toxicity tests with several common drilling fluid additives are given. The study is by no means complete but the procedure appears to be a reliable and meaningful approach to measuring the toxicity of most drilling fluid additives to shrimp.

INTRODUCTION

Two of the most important drilling areas for the oil and gas industry are the estuaries and offshore waters of the Louisiana and Texas Gulf Coast. During drilling operations in these areas, using water base muds free of oil, the formation cuttings are normally disposed of by adding directly to the water. With modern high-speed shale shakers, the quantity of drilling fluid associated with these cuttings is minimal, but some drilling mud is lost along with the cuttings. The components in the fluid are quickly diluted by the water until only a few parts per million of any one component exist in the vicinity of the wellsite.

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A variety of chemicals are used in water-base drilling fluids, and concentrations vary considerably depending upon the type of system being used. The major added components of most water-base muds other than water are commercial bentonite and barite. Several investigators (refs. 1,2) have shown these components to be essentially nontoxic to marine life. Barite and bentonite have been used in Gulf Coast offshore drilling since its inception in 1947. The increasing fish harvest along the Louisiana Gulf Coast as reported by Brashear (ref. 3), is further proof that these materials have not adversely affected the fish population over the past 20 years.

To reduce drilling problems and well cost, the industry is continually looking for improved drilling fluids. As any drilling fluids researcher will quickly note, there are a number of factors which must be considered prior to and during the development of any new drilling fluid system. One of these factors, which has always been important but is receiving increased attention, is the relative toxicity of the materials to be used in these systems. Their effects on humans as well as plant, animal, and marine life must be considered.

This increased awareness has prompted Milchem Incorporated to establish test facilities to evaluate the effect of drilling fluid additives or systems on marine organisms. This paper describes the adaptation of a static bioassay test utilizing Galveston Bay shrimp (littoral penaeids). The test is patterned after the Standard Methods for the Examination of Water and Wastewater, 13 ed., prepared and published jointly by American Public Health Association, Water Pollution Control Federation, and American Water Works Association.

WHY SHRIMP

Shrimp were chosen as the test organism since they are not only an important food crop but are biologically important as food for fish and other marine organisms. They are relatively abundant and generally available from live bait houses in the Galveston Bay area. In addition, they adapt quite well to a laboratory test environment.

Three littoral penaeids (brown, pink, and white) are abundant enough to be utilized profitably as food; however, for commercial catch statistics, they are grouped under one category. The approximate total Texas shrimp landings for 1973 were over 80 million pounds (ref. 4).

As reported by Becker et al. (ref. 5), littoral penaeids range the Atlantic coast from New Jersey through the Gulf of Mexico and West Indies to Uruguay. They occur in estuaries and littoral zones, predominantly on mud bottoms from the water's edge to 45 fathoms, rarely to 90 fathoms. They have an extended spawning season that probably varies in different parts of their range. Spawning occurs in deepwater and the young enter estuarine brooding grounds as postlarvae; they penetrate into low salinity shallow water and grow rapidly in the warmer months. As shrimp grow, they move gradually to deeper, saltier water and eventually return to the sea. A study of the time of emigration of brown shrimp from the Galveston Bay System by Trent (ref. 6) showed two peak periods, the first in May and the second in June. His study also showed the size of the emigrating shrimp increased significantly as the season progressed.

SHRIMP SOURCE

Both white shrimp *(Penaeus setiferus)* and brown shrimp *(Penaeus aztecus)* have been used in the test program. These are obtained from live bait houses near San Leon and Galveston, Texas. Twenty-gallon plastic drums fitted with battery powered aerators and filled with Galveston Bay water are used to transport the shrimp back to the Houston laboratory. At the laboratory they are transferred to a 150-liter holding tank which is filled with Galveston Bay water collected at the same time and same location as the shrimp.

On the first trip for shrimp, the 150-liter holding tank was filled with synthetic seawater prepared with "Instant Ocean Sea Salt"* and Houston tapwater. Transferring the shrimp from the relatively cold baywater (50°F) to the synthetic seawater at 68°F, the latter having equilibrated in the laboratory overnight, resulted in a loss of over 50 percent of the supply. There was also a considerable difference in pH of the two waters, a 7.4 pH for the baywater as compared to 8.0 for the synthetic seawater. This difference in pH may also have contributed to the high death rate. On the next trip for a new shrimp supply, sufficient baywater was obtained for the holding tank and the test aquariums. All tests have since been run in the baywater as there is no particular problem in obtaining a sufficient volume of this water for the tests. Sudden temperature changes and variations in pH and salinity are thus avoided, and the shrimp are kept in their natural water environment.

Though baywater is still being used, acclimatization tests have been made in synthetic seawater in which the temperature, salinity, and pH were adjusted to that of the baywater. With these adjustments, the shrimp survival rate has been good, and there appears to be no particular problem in using the synthetic seawater for the bioassay test.

LABORATORY AND TEST EQUIPMENT

The test laboratory is isolated from the central air conditioning system of the main building and is equipped with a 2-ton window air conditioner to assure that the air temperature is maintained at 68°F to 70°F. To assure that the water temperature does not drop below 68°F, the aquariums are equipped with "Supreme"† 100-watt thermostatic heaters.

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*Aquarium Systems, Inc.
†Eugene G. Danner Manufacturing, Inc.

Figure 1. 36-liter aquarium with aerator, filter, and heater.

The 150-liter tank in which the shrimp are first placed is used as a holding tank and supply source for the smaller aquariums in which acclimatization and exposure period tests are conducted. The smaller aquariums hold 36 liters and are equipped with "Silent Giant"* aerators (see figure 1). During acclimatization, they are also equipped with charcoal and flow filters.

Ten shrimp were placed in each 36-liter aquarium giving 3.6 liters and 18 sq. in. per shrimp. It was soon obvious that this did not provide sufficient floor space for the shrimp. Several would crowd together in one corner resulting in fighting and the subsequent death of a number of those in the tank. As shown in figure 2, this problem was alleviated by placing fish netting in the tank, thereby greatly increasing the surface area for each shrimp to occupy as well as providing something for them to cling to. It was observed that shrimp are quite possessive to territory and prefer to remain isolated from each other. They are also cannibalistic and quickly devour any of their number that die.

During the acclimatization period, the shrimp are fed small

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*Aquarium Pump Supply, Inc.

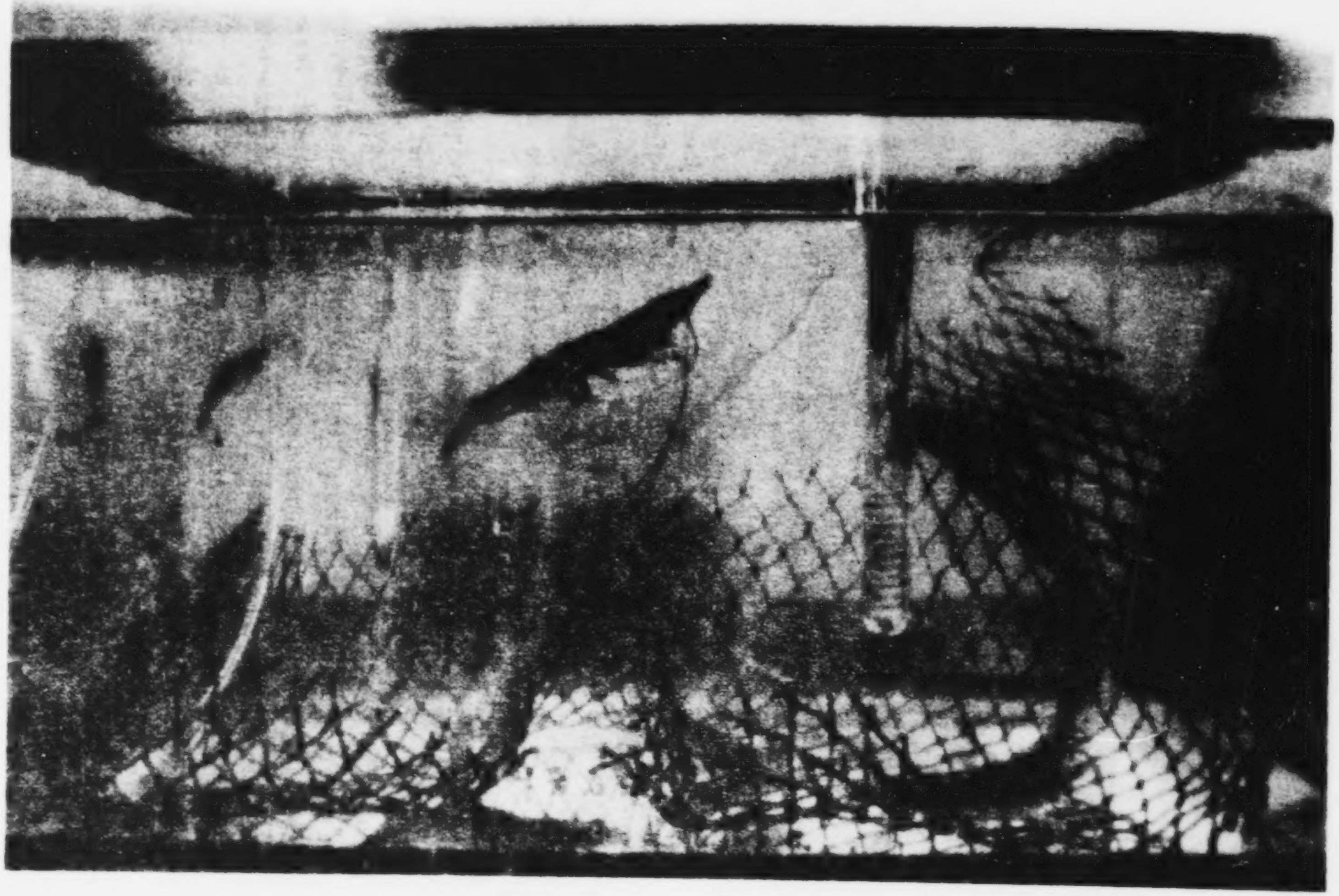


Figure 2. View of test tank with fish netting.

frozen brine shrimp. The charcoal and filter floss aid in the removal of any waste food and excretion. The Galveston Bay water is quite murky when freshly obtained but usually clears up in 2 to 4 hours with the filter operating. In some cases the water is much slower to clear, which can be due to the waste from a dead shrimp.

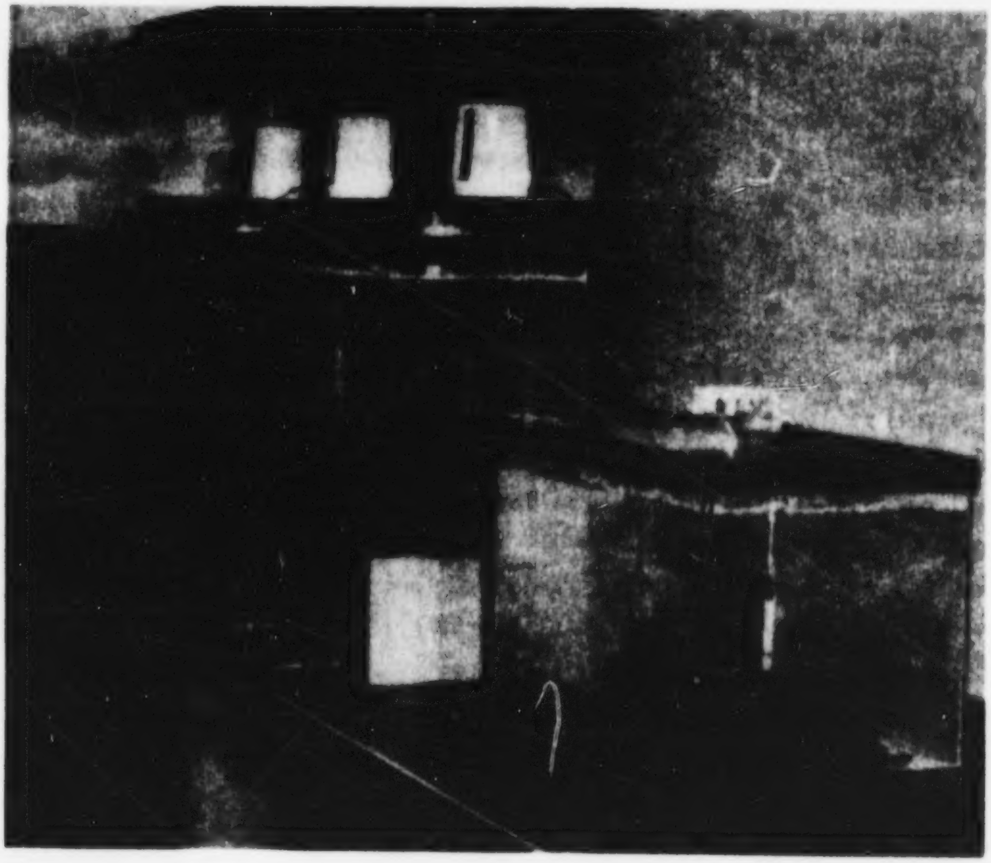


Figure 3. View of 36-liter aquariums during acclimatization.

ACCLIMATIZATION AND TESTING

To acclimatize the shrimp to the laboratory environment before exposure to the test additive, they are transferred from the large holding tank to the 36-liter aquariums. As stated above, the test tanks are filled with Galveston Bay water and the aerator and filter are operated continuously during this period. An oxygen analyzer is used to assure that the D.O. does not drop below 4.0 ppm. Six of the small aquariums are used for each test, one for control and five for different concentrations of the test chemical with 10 shrimp each. The shrimp are acclimatized in these tanks for a period of not less than 12 days. Acclimatization periods of 12 to 21 days were used. A view of several of the 36-liter test aquariums is shown in figure 3.

During the acclimatization period, the shrimp are carefully observed and the dead are quickly removed. The number of shrimp (10) in each tank is maintained constant by resupplying from the large holding tank. The incidence of disease and death within a period of 4 days immediately preceding the test is normally not more than 5 percent. The number of mortalities for two different acclimatization periods is shown in table 1. Note that the death rate does not stabilize to an acceptable level until after the eighth or ninth day, indicating the 10-day minimum period as stated in the Standard Method (ref. 7) is justified.

Before starting the actual static exposure period, screening tests using a few shrimp in small containers are made with various concentrations of the material to be tested. The purpose of these preliminary runs is to locate the general concentration range to be used in the 96-hour tests. Since five concentrations are tested for each run, two are chosen which, based on the screening tests, will be above the TL_{50} and two will be below.

After the acclimatization period, the shrimp are removed from the test tank for a brief period until the chemical to be tested is added. The material to be tested is thoroughly mixed in the water

Table 1

Run A: Mortalities for 12-day acclimatization period

Date	Number of mortalities					
	Test Tank #1	Test Tank #2	Test Tank #3	Test Tank #4	Test Tank #5	Test Tank #6
10-24-74	0	1	0	0	2	0
10-25-74	0	2	4	4	3	1
10-26-74	1	2	2	0	1	3
10-27-74	0	2	1	0	0	1
10-28-74	0	0	1	1	2	0
10-29-74	0	0	3	0	0	2
10-30-74	0	1	1	1	1	0
10-31-74	2	0	0	0	0	0
11-1-74	0	1	1	0	0	0
11-2-74	0	0	0	1	0	0
11-3-74	0	0	0	0	0	0
11-4-74	1	1	0	0	0	1

Run B: Mortalities for 14-day acclimatization period

Date	Number of mortalities					
	Test Tank #1	Test Tank #2	Test Tank #3	Test Tank #4	Test Tank #5	Test Tank #6
12-16-74	2	0	3	3	0	0
12-17-74	1	3	1	0	2	1
12-18-74	2	2	1	0	0	1
12-19-74	0	0	0	0	1	1
12-20-74	0	0	0	0	0	2
12-21-74	0	0	0	0	0	0
12-22-74	0	0	0	0	0	0
12-23-74	0	0	0	0	0	0
12-24-74	2	2	1	1	1	0
12-25-74	1	0	0	1	0	0
12-26-74	0	0	0	0	0	1
12-27-74	0	0	0	0	0	0
12-28-74	0	0	0	0	0	0
12-29-74	0	0	0	0	0	0

to assure good dispersion or solution, but violent agitation or vortexing is avoided to prevent foaming or frothing in the tank. During this interval the shrimp are held in a secondary tank having the same acclimatization conditions. Great care is required in the removal and return of the shrimp to assure that none are injured. They are removed with soft, fine mesh nets and are returned to the same aquarium from which they were taken. If one should be dropped or injured, it is replaced by one from the large holding tank. The shrimp are not fed for 3 days before the static testing is begun, nor are they fed during the 96-hour exposure period. This is to avoid large fluctuations in their metabolic rate and fouling of test solutions with metabolic waste products and uneaten food. The charcoal and flow filters are not used during the run and the air from the aerators is reduced to a fine stream of bubbles with pincher clamps.

The shrimp are carefully observed during the first hours of exposure since this is a critical period for them. Mortality checks are made and recorded at 24, 48, 72, and 96 hours. When the material tested forms a clear or transparent solution, the checks are relatively simple. In cases where the water is darkly colored with high concentrations of materials such as tannins or lignosulfonates, only those shrimp near the glass wall (figure 4) can be seen clearly enough to determine their condition; therefore, it becomes necessary to carefully remove the shrimp for an accurate count.

CALCULATIONS

The results of the bioassay tests are expressed with the term "tolerance limit" (TL) as outlined in the Standard Method (ref. 7). By definition, a 96-hour TL_{50} of a test material is that concentration in which 50 percent of the fish survive for 96 hours. The TL_{50} is equivalent to the median tolerance limit (TL_m). The 96-hour TL_{50} is estimated by plotting the data on semilogarithmic coordinate paper with concentrations on the logarithmic and percentage survival on

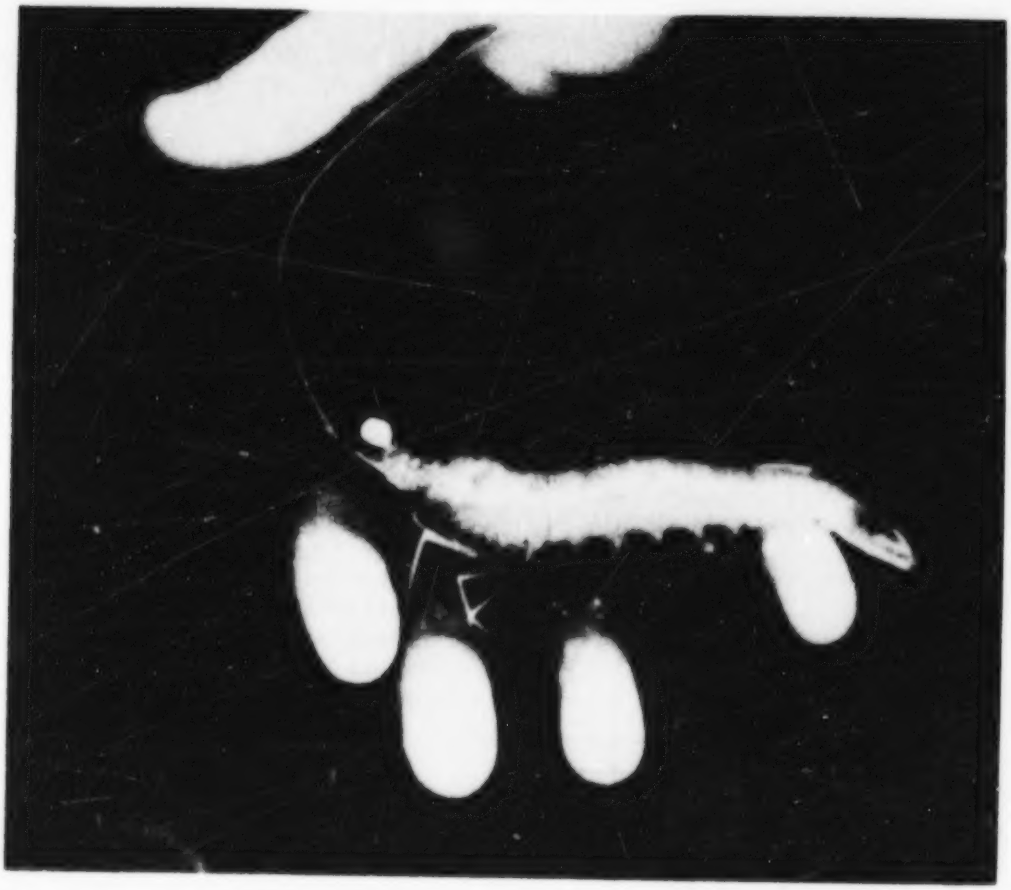
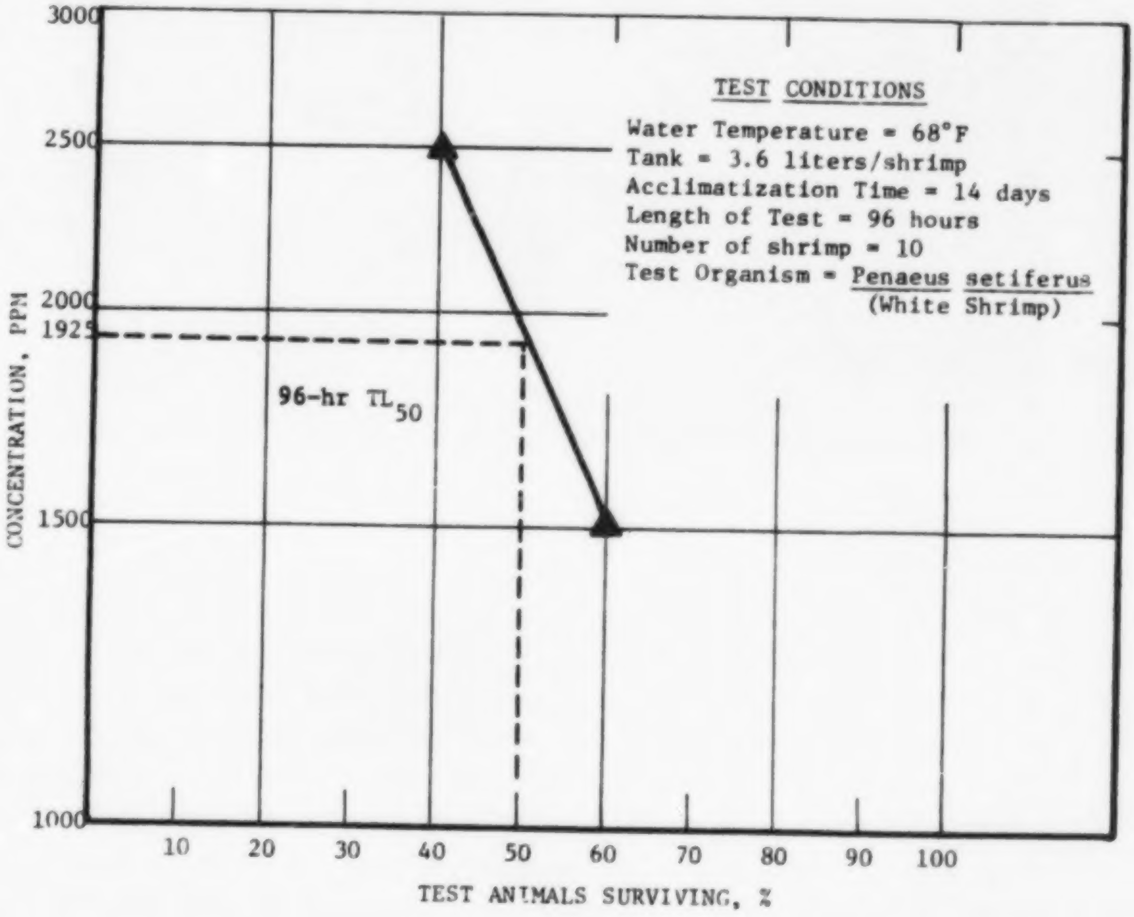


Figure 4. Inspection of shrimp in darkly colored water.

the arithmetic axis. A straight line is drawn between two points representing survival at two successive concentrations, one which was lethal to more than half and one which was lethal to less than half the shrimp. Thus the TL_{50} is an interpolated value rather than a determined value by an actual test of that specific concentration. It is important that data points be obtained below and above the TL_{50} value. An example of this graphical computation and the corresponding data is shown in figure 5.

COMPUTATION OF TL_{50}

Concentration	No. of Shrimp	Tank No.	Number of Test Animals Surviving			
			24 hrs.	48 hrs.	72 hrs.	96 hrs.
400 ppm	10	1	10	10	10	10
800 ppm	10	2	10	9	9	9
1000 ppm	10	3	10	10	9	8
1500 ppm	10	4	10	9	8	6
2500 ppm	10	5	10	9	7	4
Control	10	6	9	9	9	9



TEST CONDITIONS

Water Temperature = 68°F
Tank = 3.6 liters/shrimp
Acclimatization Time = 14 days
Length of Test = 96 hours
Number of shrimp = 10
Test Organism = *Penaeus setiferus* (White Shrimp)

Figure 5.

The authors are aware of other terms used in reporting toxicity data such as "lethal dose" (LD) and "lethal concentration" (LC). In addition, there are more sophisticated methods for calculating these values such as the use of logarithmic-probability graph paper and the more refined methods of probits (ref. 8) and logits. The simpler method of calculation was used since it appears to be quite adequate for materials tested thus far.

NINETY-SIX-HOUR TL_{50} RESULTS

Two common types of drilling fluid additives which serve as deflocculants are tannin and lignosulfonates. The 96-hour TL_{50} for an iron-modified Hemlock Bark extract (tannin), a chrome-treated lignosulfonate, and an iron-lignosulfonate are shown in table 2. As will be noted, the modified Hemlock Bark extract shows the lowest tolerance limit and the iron-lignosulfonate the highest. It should be pointed out that the chrome in the chrome-treated lignosulfonate

Table 2. Ninety-six-hour TL_{50} values for several drilling fluid additives

Additives	Test organism	96-hr TL_{50}, ppm
Modified hemlock Bark Extract	White shrimp (Penaeus setiferus)	265
Chrome-treated lignosulfonate	White shrimp (Penaeus setiferus)	465
Iron-lignosulfonate	White shrimp (Penaeus setiferus)	2,100
Nonwater dispersable defoamer	Brown shrimp (Penaeus aztecus)	Eratic
Low molecular wt. polyacrylate	White shrimp (Penaeus setiferus)	3,500
Cellulosic-calcium carbonate workover additive	White shrimp (Penaeus setiferus)	1,925

is present as trivalent chromium, and no hexavalent or unreduced chromium is present. Neither the modified bark extract or the iron-lignosulfonate contain any significant amount of chromium.

A lignosulfonate concentration of 200 to 300 ppm will impart a distinct brown color to water. The principal author has observed numerous drilling sites in water locations over the past 20 years in which lignosulfonate muds were being used. In not one of these has the lignosulfonate content been present in sufficient quantity on the cuttings to produce a visible coloration of the water.

As is well known by drilling fluids engineers and technicians, mud additives range from high water solubility to nonwater dispersability. One such nonwater dispersable compound which is used as a defoamer was tested with the bioassay procedure. Shrimp mortalities were very erratic as they had to penetrate the surface before coming in contact with the compound. Only relatively small concentrations of these type materials are used and the possibility of getting any significant amount on the water surface in actual use conditions is practically nil. This test did point out however, that it may be desirable to employ some slight surface agitation when testing materials of this nature in order to produce surface movement as would occur under natural conditions.

The results obtained with an acid-soluble workover additive are also shown in table 2. Note that the TL_{50} was 1925 ppm. This material is composed essentially of graded calcium carbonates and a high molecular weight cellulosic polymer. It is designed to impart viscosity to the workover system and at the TL_{50} concentration imparts a measurable viscosity increase to the water in the test tank. This viscosity effect may have influenced the mortality rate of the shrimp in addition to any toxicological effects from the additive. It would be highly unlikely that a concentration approaching the TL_{50} value for the material would ever be encountered in the water surrounding the workover operation.

The TL_{50} for a low molecular weight polyacrylate as shown in table 2 was found to be 3,500 ppm. This particular compound has a molecular weight below 5,000. Much higher molecular weight polyacrylates are also used in drilling fluids, and it would be interesting to see how their TL_{50} values compare with low molecular weight ones.

The tests run thus far have covered only a small number of the chemicals used in oil well drilling fluids. Additional materials are scheduled and those will be run as time permits. The procedure is time consuming, but to use shortcuts and haste would likely affect the reliability of the data. Only individual mud components have been run thus far though it is planned to test whole muds to determine if any synergism of components exists.

In general, it can be concluded that with the modifications and additions that have been made, the test method is a satisfactory means for determining the acute toxicity of drilling fluid additives to Galveston Bay shrimp. The data, of course, cannot be extrapolated to other marine species or other habitats but should serve as a useful tool in the selection of compounds for new drilling fluid additives.

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ACUTE TOXICITY OF WELL-DRILLING MUDS TO RAINBOW TROUT, *Salmo Gairdneri* (Richardson)

R. H. Weir and B. Moore*

Abstract

The acute toxicity of drilling muds to rainbow trout (Salmo gairdneri) was investigated under 96-hour static bioassay test conditions for a Canadian Arctic exploratory well. Samples were taken at various well depths and tested at various concentrations to determine the lethal concentration to 50 percent of the test population in 96 hours (96 hr LC_{50}*). In the sample series it was found that the toxicity could be grouped as to its relationship with the active mud system and the depth at which the sample was taken. Results of the toxicity analyses defined three distinct groups of toxicity. The first toxicity group exhibited an* LC_{50} *value of <20 percent mud concentration by volume. The dominant toxic factor being the high level of KCl that was used in drilling the surface portion of the hole. The second toxic group exhibited* LC_{50} *values in the range of 36 to 70 percent mud concentration by volume. The toxicity of this group was characterized by the lack of a dominant chemical or physical toxicant. The toxic action appeared to be the result of the combination of the drilling components present within the unweighted mud system (8.8 - 9.3 lb/gal). The third toxic group exhibited* LC_{50} *values of 9 to 16 percent mud concentration by volume. Toxicity characterization was generally a continuation of the multifactor toxicity of group two, but at a much higher toxic level due to the increase in solids and viscosity that are associated with weighted muds.*

INTRODUCTION

The potential water pollution problems associated with the handling and disposal of drilling fluids in Canada's Arctic regions is of relatively recent concern. With the advent of onshore drilling in the flood plains of the Mackenzie Delta in the late 1960's and the commencement of offshore drilling in the shallow regions of the Beaufort Sea, Hudson Bay, and the Arctic Ocean in 1974-75, an industry/government research program was established in March 1973. The purpose of this program was to investigate the magnitude of the pollution problem associated with current methods of handling sump fluids from onshore exploratory drilling locations and the disposal of waste drilling fluids from offshore exploratory operations.

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For the past 2 years, the Environmental Protection Service's Aquatic Toxicology Laboratory, Edmonton, Alberta, tested drilling waste discharges from 10 Canadian Arctic wells for acute toxicity to rainbow trout (*Salmo gairdneri*) under 96-hour static bioassay conditions. Rainbow trout were selected as the test organisms as current Federal Government environmental regulations and guidelines recognize rainbow trout as the standard bioassay test organism.

For the purpose of this paper, data from a single well in the Beaufort Sea area (figure 1) are presented. The well is fairly typical for the Beaufort Sea area in that a water base KCl-gel-polymer mud system was used for the surface hole section, a water base gel-polymer mud system was used for the unweighted section of the hole and a gel-barite weighted system was used for the lower portion of the well.

This paper examines the relationship between the acute toxicity of the samples, expressed as 96-hour LC_{50}* values, and the type of mud system used.

MATERIALS AND METHODS

Sample Collection

The drilling mud samples were collected in two 25-gallon polyethylene-lined barrels. After collection, the samples were shipped to the Environmental Protection Service, Aquatic Toxicology Laboratory, Edmonton, by the fastest means available. Upon receipt, all samples were stored at 4°C until tested. Table 1 lists the dates, depth of hole at sampling, and the sample site in the mud system for each sample.

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*Sample concentration (percent sample by volume) that kills 50 percent of the test rainbow trout in 96 hours.

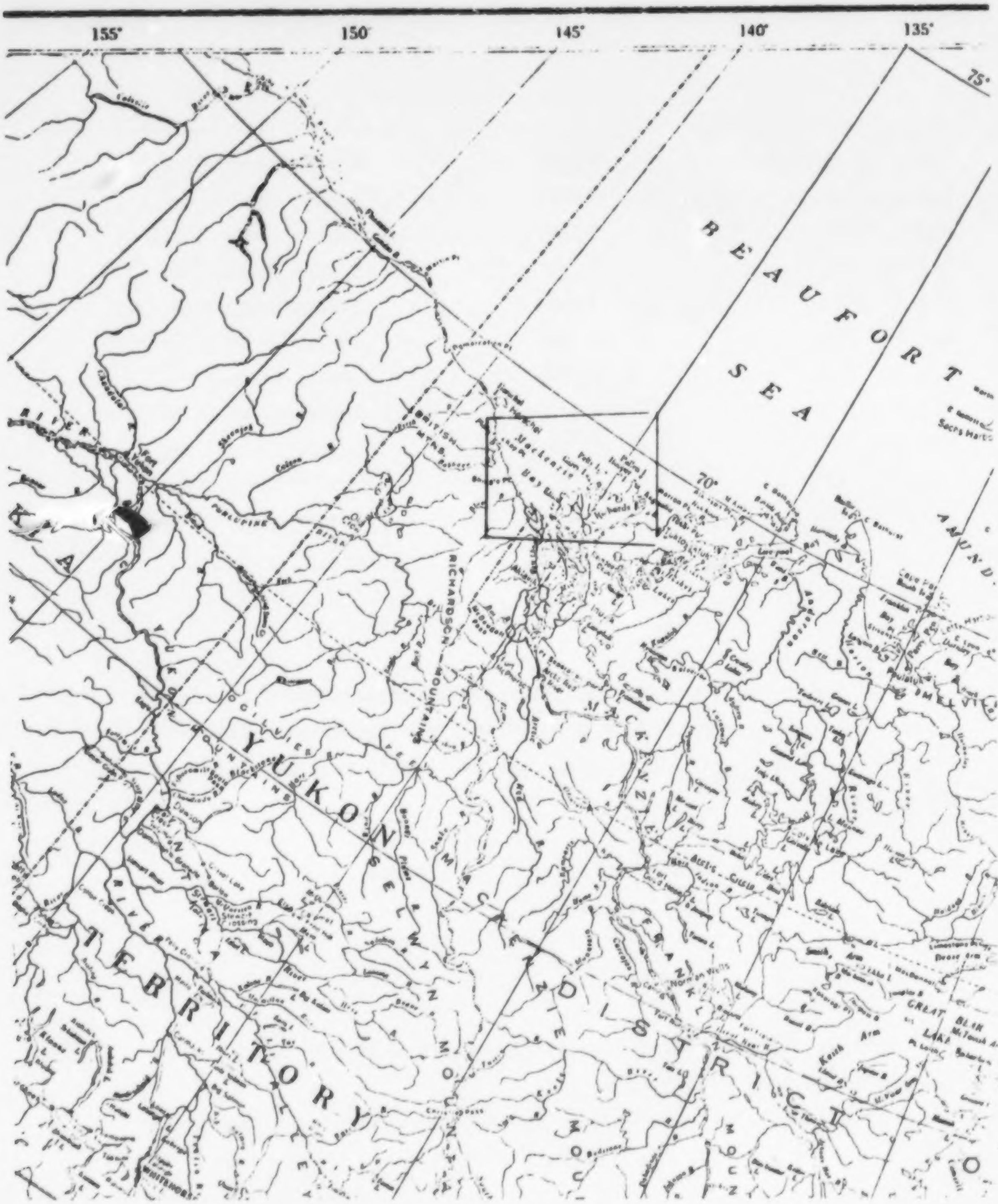
155°
150°
145°
140°
135°
75°
70°
BEAUFORT SEA
AMUND
YUKON TERRITORY
MACKENZIE DISTRICT
BRITISH MTNS.
RICHARDSON MOUNTAINS
OGILVIE MOUNTAINS
SELWYN MOUNTAINS
MACKENZIE MOUNTAINS
PORCUPINE RIVER
YUKON RIVER
Mackenzie Bay
Dawson
Norman Wells
GREAT BEAR LAKE

Figure 1. Beaufort Sea area.

Table 1. Sample series data

Date	Depth (ft)	Sample site
April 25, 1974	3,000	Shaker Under Flow
May 4, 1974	4,000	Shaker Under Flow
May 5, 1974	5,000	Shaker Under Flow
May 6, 1974	6,000	Shaker Under Flow
May 7, 1974	7,000	Shaker Under Flow
May 10, 1974	8,000	Shaker Under Flow
May 12, 1974	9,000	Shaker Under Flow
May 16, 1974	10,000	Shaker Under Flow
May 27, 1974	11,000	Shaker Under Flow
June 3, 1974	12,000	Shaker Under Flow
June 15, 1974	13,000	Shaker Under Flow

Testing Procedures

The water used for both the holding and acclimation of the fish stocks and the diluent used in performing the bioassays was received as Edmonton City water. This water was treated to maintain the following characteristics:

pH	7.0 - 8.0
Hardness ($CaCO_3$)	70 - 80 mg/l
Total Residual Cl_2	<0.01 ppm
Free Cl_2	<0.01 ppm
Temperature	10° ± 1° C.

Table 2 lists the experimental parameters that were maintained during the testing program.

Mortality checks were made at the following times: 0.25, 0.50, 1.0, 2.0, 4.0, 8.0, 12, 24, and every subsequent 12 hours up to a total

Table 2. Test parameters

Parameter	Level
Test volume	40 litres
Test pH*	6.0 - 9.5
Test temperature	15° C ± 1.0° C
Dissolved oxygen	>6.0 mg/l (by aeration)
Fish species	*Salmo gairdneri* (Richardson)
No. of fish/concentration	8
Loading densities	>2.0 l/gm/expt.
Photoperiod	12 hour light/12 hour dark

*Adjusted by reagent grade HCl or NaOH.

of 96 hours. During the first 8 hours, the checks were made as frequently as possible to insure that the individual times of mortality were recorded.

Death was regarded as the cessation of all movement by the fish for greater than 1 minute, even after prodding. Dead fish were removed immediately and the time of death recorded. The weight and fork length of each fish was measured and recorded. At the end of the experiment, all remaining fish were killed and measured.

Chemical monitoring of the bioassay tests involved regular 12-hour checks for dissolved oxygen, pH, temperature, and conductivity throughout the 96 hours or until all of the fish died in the concentration.

Raw data was in the form of percent mortality at each mortality check for each concentration. Using the methods of Litchfield (ref. 1), this data was plotted as cumulative percent mortality vs. time on probit-log graph paper and the best eye-fitted line was drawn if three or more points were available. The point where the line intersected 50 percent mortality was read as the median lethal time* (LT_{50}) and, where possible, 95 percent confidence limits were calculated for this value.

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*Median lethal time (LT_{50}) is the mean time to 50 percent mortality of a population in a single concentration. The term mean survival time (MST) is equivalent.

For each experiment where two or more concentrations had LT_{50} values, these values were plotted vs. concentration on log log graph paper (ref. 2) and an eye-fitted line was drawn to 96 hours. The 96-hour LC_{50} was read at this point.

All data was processed on a Hewlett-Packard 9.830A Data System.

RESULTS

Field sample data for the well, as reported by the operator, are presented in table 3. Included are the depth at time of sampling and the corresponding values for solids (% vol.), calcium (mg/l), and chloride (mg/l).

Bioassay test results are listed in table 4. The data reported includes the depth of hole at sampling, test concentrations of the sample as percent sample by volume, LT_{50} and 95 percent confidence limits, Litchfield slope, and LC_{50} range as well as the LC_{50} derived from the plotted data. The LC_{50} values were compared with the depth of the hole to produce a toxicity profile (figure 2). Conductivity and chloride levels were also plotted in relation to depth and a definite trend was exhibited (figures 3 and 4). These trends were compared to the toxicity profile to show possible correlations with the toxicity of the samples.

The three types of mud systems used in drilling the well (surface, unweighted, and weighted) were related to the toxicities of the samples to attempt a correlation as to component group and toxicity.

DISCUSSION

In this testing program it was found that the acute toxicity of the drilling fluids tested was directly related to the different types of mud systems used.

The initial mud system that was used was a KCl-gel-polymer mud. This mud was used for the surface portion of the hole to a depth of 3,000 feet. The 3,000-foot sample was very toxic, having an LC_{50} of

Table 3. Field sample data

Depth (ft)	Solids (% vol.)	Ca (mg/l)	Cl (mg/l)
3000	5.0	1,000	16,500
4000	3.5	750	5,600
5000	5.0	500	4,600
6000	5.75	150	4,500
7000	5.0	50	4,100
8000	5.25	50	3,700
9000	6.0	75	3,400
10000	7.0	75	2,600
11000	7.0	75	2,000
12000	16.0	0	1,750
13000	39.0	0	1,850

10 percent by volume (table 4). Corresponding to this high toxicity value, high values for chloride, calcium, and conductivity (table 3, figure 3) were noted. These high levels, especially the chloride, when related to the low LC_{50} value and very short LT_{50} times at 60 percent and 40 percent suggest that the primary toxic component was the KCl. Beckett et al. (ref. 4) report that KCl and the polymer components were toxic at similar levels (i.e., LC_{50} 1,800-2,000 mg/l). However, with the estimated higher amounts of the KCl in this mud system, one could conclude that it contributed the most to the toxicity in this mud. The gel having a reported LC_{50} value of 10,000 mg/l (ref. 4) would have some, but not a major toxic effect on the sample, as solids values were moderate (table 3).

With the change of mud systems from a KCl-gel-polymer system to an unweighted gel-polymer mud at the 4,000-foot sample a five- to six-fold decrease in toxicity was observed. This was likely due to the elimination of the KCl with the resultant drop in chloride (figure 4) and conductivity (figure 3) values. The LC_{50} value decreased to 55 percent.

Samples from 4,000 feet through to 9,000 feet exhibited the toxic

Table 4. Bioassay results

Depth (ft.)	Conc. (%/vol.)	LT_{50} (hr.) (95% confid. limits)	Litchfield slope	LC_{50} (%/vol.)
3,000 Surface hole mud	60	0.22(0.14 - 0.34)	1.59	Range <20 Plotted 10%
	50	1.45(1.38 - 1.52)	1.08	
	40	10.5 (7.3 - 15.0)	1.70	
	30	15.0 (10.3 - 21.8)	1.72	
	20	33.0 (25.2 - 43.2)	1.47	
4,000 Unweighted middle hole mud	100	0.23(0.21 - 0.25)	1.12	Range $40<LC_{50}<60$ Plotted 55
	80	1.15(0.74 - 1.78)	1.89	
	60	40.0(26.5 - 60.5)	1.82	
	40	–	–	
	20	–	–	
5,000	100	0.15(0.13 - 0.18)	1.28	Range $20<LC_{50}<40$ Plotted 39
	80	0.40(0.32 - 0.50)	1.39	
	60	7.20(4.50 - 11.40)	1.96	
	40	75.0(54.0 - 104.1)	1.59	
	20	–	–	
6,000	100	0.22(0.10 - 0.46)	3.03	Range $60<LC_{50}<80$ Plotted 70
	80	15.5(6.79 - 35.38)	3.33	
	60	–	–	
	40	–	–	
	20	–	–	
7,000	100	0.10(0.08 - 0.12)	1.30	Range $40<LC_{50}<60$ Plotted 50
	80	0.16(0.11 - 0.23)	1.68	
	60	0.77(0.46 - 1.28)	2.08	
	40	–	–	
	20	–	–	
8,000	100	0.11(0.09 - 0.13)	1.32	Range $40<LC_{50}<60$ Plotted 55
	80	1.45(0.24 - 8.64)	–	
	60	39.0(32.4 - 49.9)	1.30	
	40	–	–	
	20	–	–	

continued

Table 4. Bioassay results (con.)

Depth (ft.)	Conc. (%/vol.)	LT_{50} (hr.) (95% confid. limits)	Litchfield slope	LC_{50} (%/vol.)
9,000	75	14.5(8.39 - 25.05)	2.22	Range $30<LC_{50}<45$ Plotted 36
	60	31.0(23.77 - 40.44)	1.47	
	45	45.0(30.9 - 65.4)	1.70	
	30	–	–	
	15	–	–	
10,000 Weighted bottom hole mud	75	0.29(0.23 - 0.36)	1.37	Range $15<LC_{50}<30$ Plotted 16
	60	8.0(2.8 - 22.9)	2.94	
	45	23.0(17.7 - 29.9)	1.45	
	30	24.0(12.0 - 47.8)	2.04	
	15	–	–	
11,000	75	0.36(0.26 - 0.49)	1.56	Range $LC_{50}<15$ Plotted 9%
	60	5.4 (4.6 - 6.3)	1.18	
	45	6.8 (5.4 - 8.5)	1.27	
	30	11.5 (7.7 - 17.3)	1.79	
	15	32.0(26.1 - 39.2)	1.33	
12,000	50	8.2(7.1 - 9.5)	1.24	Range $10<LC_{50}<20$ Plotted 15
	40	9.8(8.1 - 11.9)	1.33	
	30	10.5(7.6 - 14.4)	1.59	
	20	62.0(16.3 - 235.9)	4.76	
	10	–	–	
13,000	50	7.0(6.4 - 7.6)	1.14	Range $LC_{50}<10$ Plotted 9
	40	7.4(6.6 - 8.3)	1.18	
	30	9.1(7.9 - 10.4)	1.21	
	20	19.5(15.8 - 24.0)	1.35	
	10	63.0(44.5 - 89.2)	1.59	

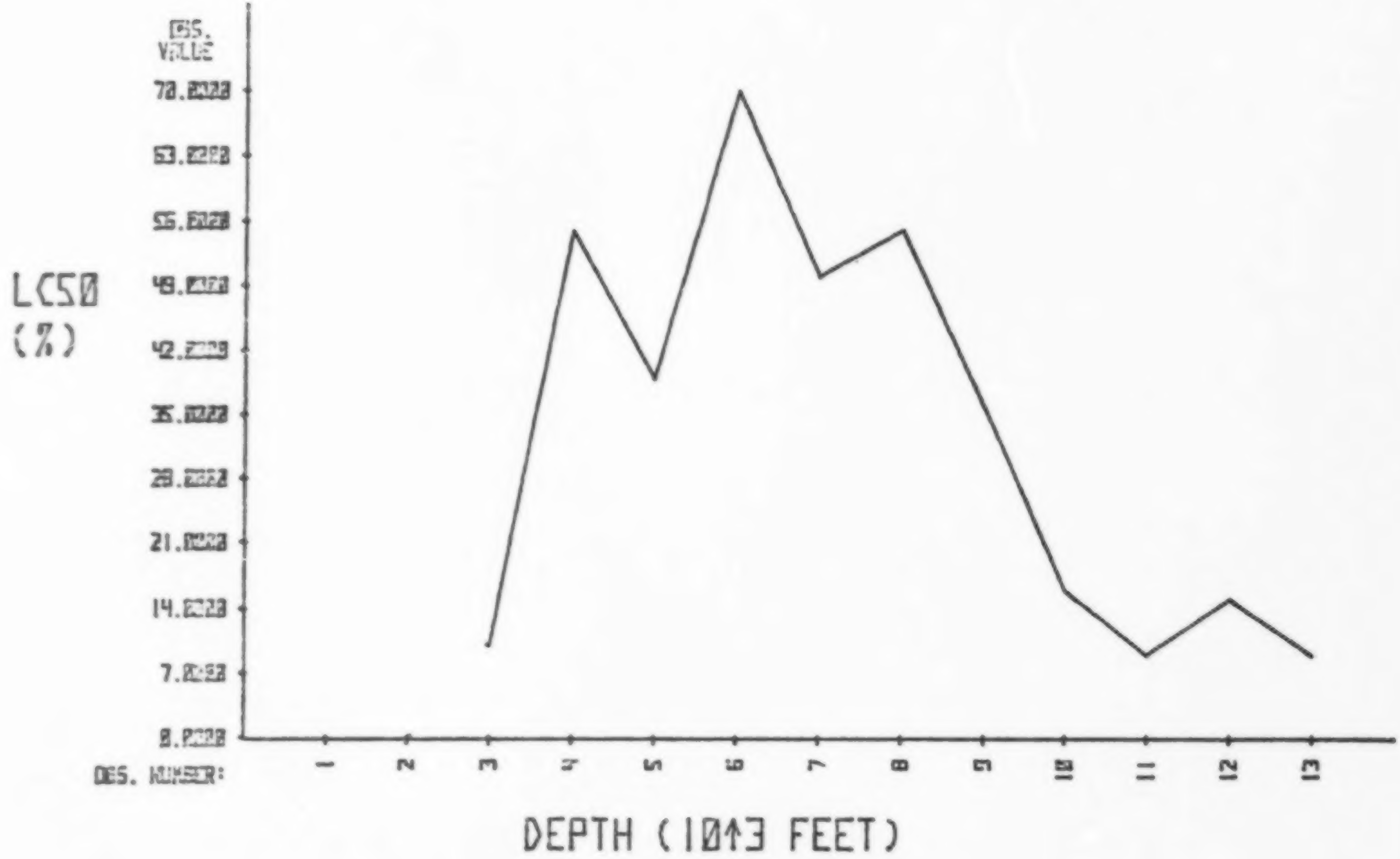

Figure 2. Toxicity vs depth.

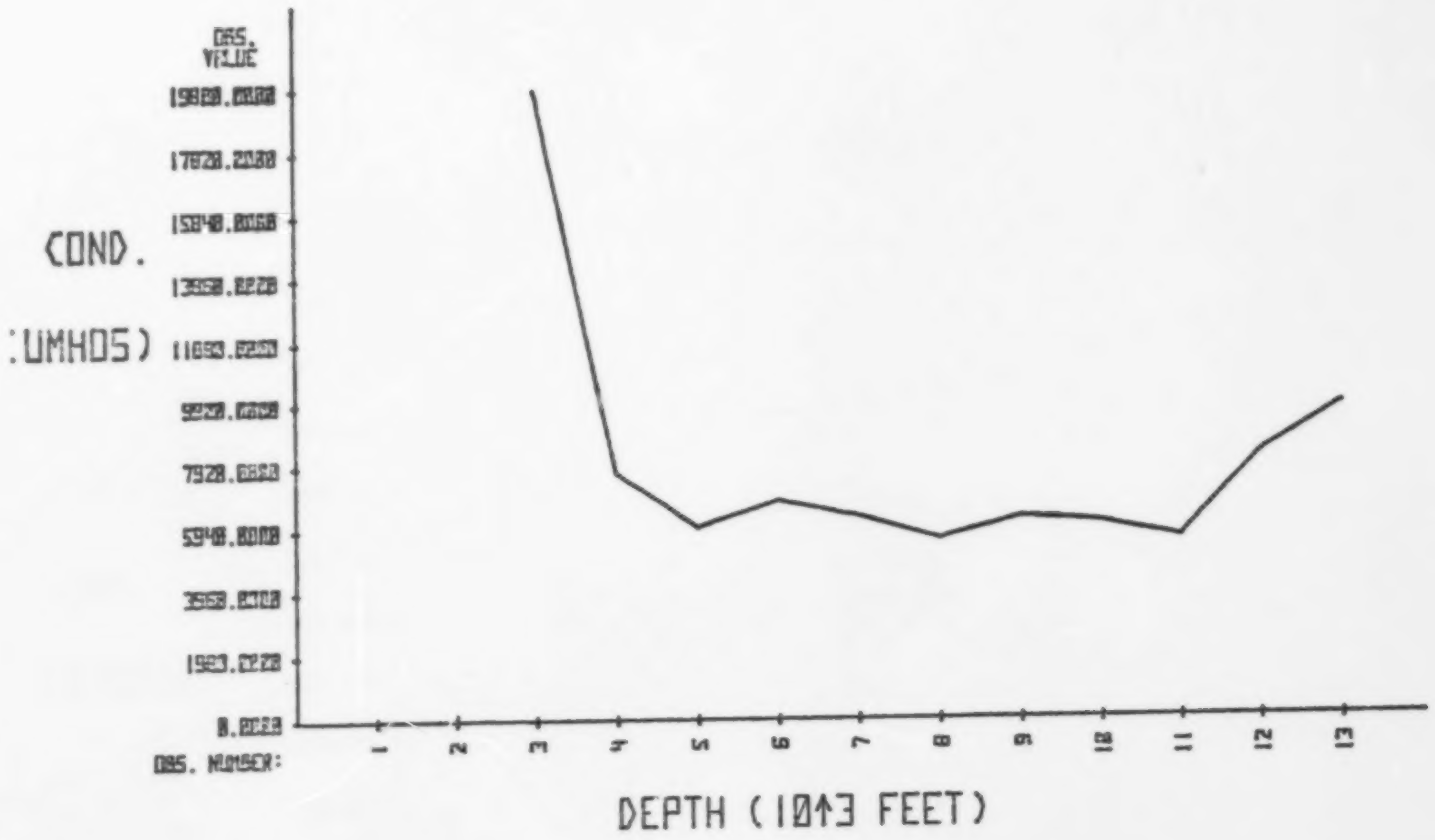

Figure 3. Conductivity vs depth.

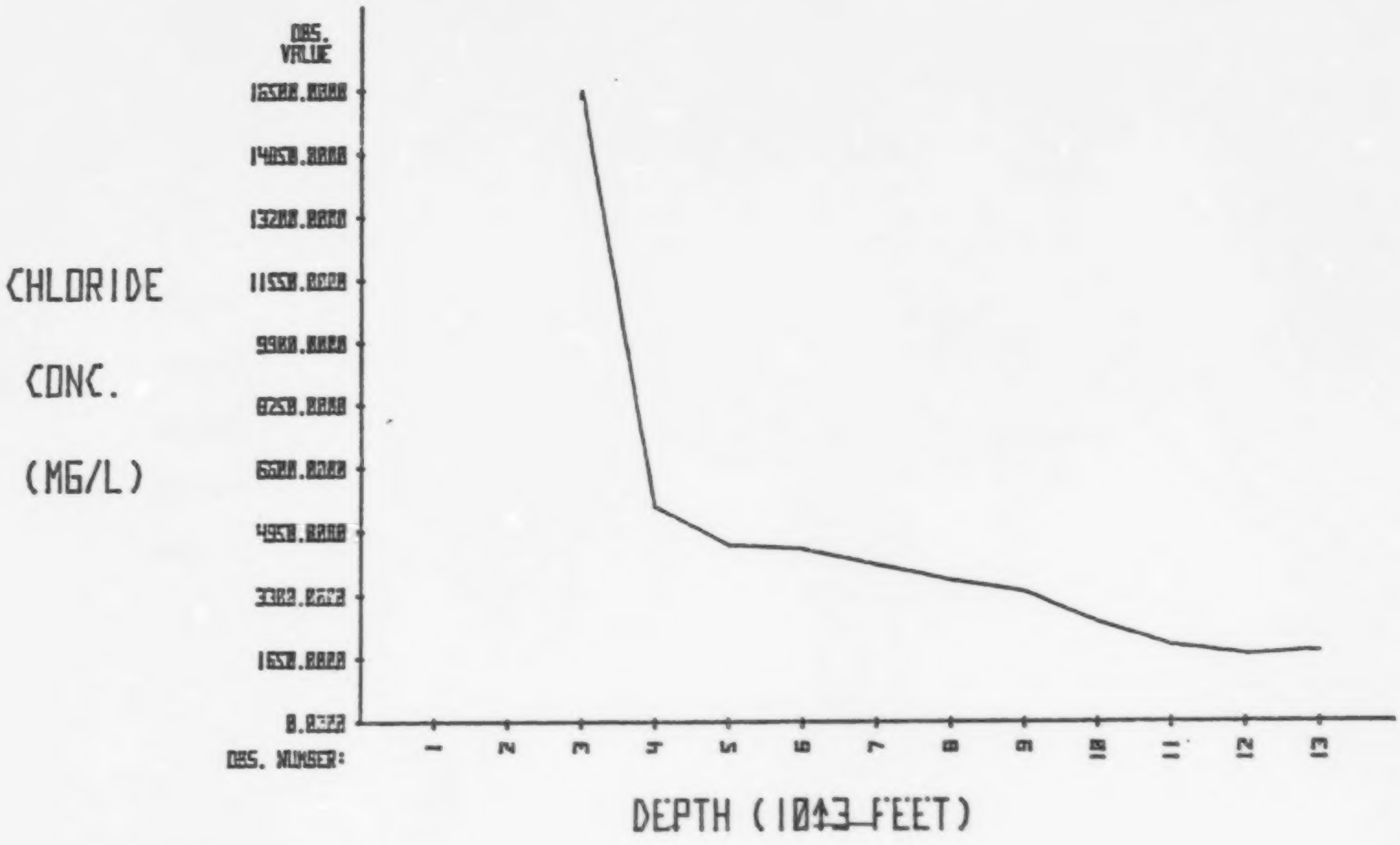

Figure 4. Chloride concentration vs depth.

properties of this unweighted gel-polymer mud. The samples still remained acutely toxic to the trout as the samples still contained enough gel and polymer to exert a toxic influence. This was clearly evident at the 100 and 80 percent concentrations as noted by the extremely short LT_{50} values. However, the toxicity profile of this mud system can be described as moderately toxic with some variation (figure 2). No single toxic agent was in high enough concentration to predominate. Each of the chemical and physical mud parameters involved contributed towards the acute toxicity either separately, or in combination. The precise characterization of these relationships was beyond the scope of this study.

The third mud system, a weighted gel-barite system, was used during the 10,000- to 13,000-foot samples. As a result, solids values increased (table 3) resulting in a corresponding increase in acute toxicity. The LC_{50} values of 9-16 percent were considerably lower than those of the unweighted mud system. The increase in mud viscosity and solids content is evident in that the samples had to be diluted to 75 or 50 percent (table 4) before the trout could be introduced to the sample. (A slight increase in conductivity was noted, and calcium and chloride levels decreased.) In general, the particulate suspended solids are known to exert their influence through abrasion and erosion of sensitive gill tissues (ref. 3). The associated viscosity used to support the solids appeared to exert its toxic influence by way of mechanical suffocation in higher test concentrations (ref. 4).

pH was not a significant source of toxicity in any of the samples. As these muds characteristically have pH values in excess of 9.5, pH adjustment of the sample to the range 6.0 to 9.5 was made to minimize the potential for pH toxicity.

Due to the lack of adequate and reliable mud composition data, mud component usage data, and replicate tests, further discussion as to the toxic properties of the muds, their components, and their action cannot be made.

In conclusion, the overall acute toxicity trend from the surface to bottom hole was for a shift from a high KCl-related toxicity to a moderate multifactor toxicity with a final high toxicity as a result of a high solids effect.

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BACTERICIDES USED IN DRILLING AND COMPLETION OPERATIONS

T. J. Robichaux*

Abstract

Bactericides are often added to drilling muds and completion fluids to prevent microbial degradation of organic additives and to suppress the formation of H_2S *by SRB. Of all possible additives, bactericides are the only ones which require registration with the Environmental Protection Agency. Efficacy, treating dosages, and environmental effects must be substantiated for registration. The chemical types of bactericides used are aldehydes, chlorinated phenols, quaternary amines, and alkyl amines. Of the several methods by which bactericides can enter the environment from drilling operations, mud and packer fluid disposal present the major mechanism. Because bactericides are made and used to kill living organisms, it is correct to expect them to be hazardous to other living creatures--such as fish and birds. By using proper cautions, the environmental hazards can be minimized. If bactericides used in drilling and completion do enter the environment, most will be removed by natural processes.*

INTRODUCTION

Drilling fluids are usually a complex mixture of inorganic and organic materials added together to enable the mud to perform multiple functions. Table 1 is a listing of typical additives and their individual functions. Particularly in water base and low solids muds, the organic materials are subject to attack by microorganisms which are introduced into the mud with the water phase. The microorganisms of concern to drilling are aerobic bacteria which convert organic

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Table 1. Drilling fluid additives and their primary functions

barium sulfate ($BaSO_4$)	weighting agent
caustic ($NaOH$, Na_2CO_3, etc.)	pH adjustment
calcium compounds (CaO,$Ca(OH)_2$, $CaCl_2$,$CaSO_4$,$2H_2O$)	conditioning for use in calcium formation, pH control
hydrocarbons (diesel oil, lease crude oil)	fluid loss control, lubrication
sealants (scrap, cellulose, rubber, etc.)	seal against leakage to formation.
thinners (tannins, lignosulfonates, quebracho, lignins, etc.)	dispersion of mud solids
emulsifiers (lignosulfonates, alkyl ethylene oxide adducts, hydrocarbon sulfonates)	forming oil-in-water or water-in-oil emulsions
bactericides (substituted phenols, formaldehyde, amines, etc.)	protection of organic additives against bacterial decomposition.
fluid-loss control additives	reduction of fluid loss to formation

molecules to cell structure, carbon dioxide, and water. Such microbial degradation reduces or destroys the effectiveness of the additive and spoils the rheological properties of the fluid.

Sulfate-reducing bacteria (SRB) are specific microbial organisms which grow under anaerobic conditions and derive their source of energy by reducing sulfates and materials containing oxidized sulfur with the concurrent production of hydrogen sulfide. These bacteria are widely distributed in nature and can be inadvertantly added to drilling or packer fluids in water used in the fluids. If such contaminated water is injected into the producing formation, the bacteria may grow and produce corrosive amounts of hydrogen sulfide. If the water is left as a packer fluid and contains sulfates, bacterial growth may occur, adding to the corrosion problems in the tubing and casing annulus.

BACTERICIDES AS FLUID ADDITIVES

To prevent bacterial growth, bactericides are frequently added to drilling and completion fluids. These additives are generally organic chemicals, such as formaldehyde, pentachlorophenol, alkyl amines, or mixtures of such chemicals. There are other methods of controlling bacterial growth, such as pH control or control of ionic strength. However, bactericide addition is the most common and most direct method. Table 2 is a list of generic types of bactericides and some examples of chemicals commonly used.

Generally, bactericides which are not cationics are used in drilling muds. These are aldehydes and phenols. They are effective against aerobic bacteria and fungi as well as against anaerobic SRB. The principal need for such agents is in (1) water base muds that contain starch, CMC, and other organic materials which are subject to microbial attack, and (2) in low solids fluids which contain sulfates.

Table 2. Types of biocides in use

• Aldehydes	- formaldehyde, paraformaldehyde, gluteraldehyde
• Chlorinated Phenols	- pentachlorophenol, alkyl dichlorophenol, sodium salts of phenols
• Quaternary Amines	- alkyl dimethyl ammonium chloride, coco dimethyl benzyl ammonium chloride
• Diamine Salts	- acetate salts of coco or tallow diamines
• Other	- caustic, alkyl phosphates, heavy metal salts

Bactericides most often used in packer fluids and completion fluids are quaternary amines or acetate salts of coco amines. These materials are most effective against SRB and also function as film-forming corrosion inhibitors. Thus, two advantages are gained by their use--hydrogen sulfide generation is suppressed, and general corrosion is inhibited.

Because bactericides are surfactants, they will have an effect on the muds to which they are added. For example, quaternary amines will cause certain clay materials to flocculate. Therefore, selection and use of bactericides should be made with an understanding of what the bactericide will do to mud properties.

Bactericide Registration

Of all the additives used in drilling fluids, bactericides are the only additive which must be registered with the Environmental Protection Agency. Bactericides are included in the laws governing pesticides--a group of chemicals which cover herbicides, sanitizers, insecticides, and rodenticides. Every manufacturer and distributor of such products must register any and all formulations for which claims of pest control are made.

EPA registration procedures require registrants to establish efficacy towards target organisms, treating schedules, and environmental hazards of products prior to registration. Literature describing the product, its safety, first aid for treating accidents, as well as specific instructions for uses must accompany the products when sold. Labels on each container specifically state the active ingredients and concentrations, the degree of potential hazard to humans, and precautions to be taken to avoid environmental hazards. This registration provides the potential user with the opportunity to tighten the use of bactericides to provide sufficient protection without overtreating in the vague hope of doing a lot of good. It also places the responsibility upon the user to take necessary precautions to prevent escape of the chemicals into the environment.

TOXIC EFFECTS OF BACTERICIDES

Bactericides are made and used to kill bacteria. Such chemicals are, therefore, potentially damaging to other living organisms. As water soluble chemicals, bactericides will be carried into the aquatic environment readily, posing a hazard to fish and birds. The hazard can become a reality in many different ways. The chemical may kill insects and larva on which fish feed, thus depleting the flood supply. The chemical may have an acute effect on fish, causing physiological damage which results in inability to swim, to escape capture by predators or in death due to poisoning. The chemical may pose a threat to birds and other wildlife by poisoning the water they drink or the insects and crustaceans which birds eat. Important to remember also is the potential hazard of bactericides to man. By introduction into the water cycle, these chemicals pose a potential threat to potable water supplies.

Compared to many other industrial chemicals, bactericides currently used for drilling and completion operations are relatively low on the hazard scale. Table 3 is a compilation of environmental data for the classes of chemicals being used. Current standards of

Table 3. Typical environmental data

Bactericide type	TL_{50} ppm (fish)	LD_{50} gm/kg (birds)	BOD_5
Aldehydes	50 - 400	5 - 15+	100
CI Phenols	0.2 - 1	5 - 15+	<20
Quats	0.2 - 5	>5	95+
Amines	0.4 - 4	>5	90 - 100
Toxaphene	0.025	---	---
LAS	3 - 4	---	100

TL = toxicity limit; LD = lethal dose; LAS = linear alkyl sulfates.

mean toxicity limit (TL_{50}) to fish and mean lethal dosage (LD_{50}) to ducks and quail, are shown compared to toxaphene, a pesticide, and linear alkyl sulfates (LAS), an ingredient in washing detergents.

Table 3 is not intended as a definitive statement of limits, but lists data drawn from several studies of toxicities of chemicals to various aquatic species. As can be seen, most bactericides in use are considerably less toxic than toxaphene and more nearly in the order of LAS detergents.

Another measure of environmental concern is the persistency of a chemical in the aquatic environment. The biochemical oxygen demand (BOD_5) values shown in table 3 are a rough measure of whether the chemical will persist. The data indicate that all are degraded to some extent by natural processes. With the exception of chlorinated phenols, all are degraded to near 100 percent of theoretical in 5 days. Toxaphene, by comparison, is a very persistent material which can accumulate in the food chain causing chronic poisoning by biomagnification.

There is no disguising the fact that misuse of mud bactericides can cause damage to the environment. However, with proper controls and use, the danger is minimized. By their chemical and biological nature, the chemicals are a relatively low level hazard.

Loss to the Environment

Several avenues exist whereby bactericides may be lost into the environment from drilling and completion operations. With the exception of spillage, most of the avenues tend to be either self-limiting or of incidental consequence. It is important to remember that bactericides are made and used to kill living organisms. They are, therefore, hazardous to other living creatures--such as fish and birds. By using proper precautions, the environmental hazards can be minimized.

The most obvious means of accidental loss of bactericides are:

- Fluid loss to a permeable zone. Bactericides will be carried with any water lost to a zone along the drilling path. Because fresh water zones are most often cased off before muds are treated, little likelihood exists for contaminating useful water zones. Water loss to other formations is generally minimized by filter cake buildup or by including fluid loss additives in the drilling fluid. After completion, all but the completed zones are cased--or cemented off in dry holes--practically eliminating return of the bactericide to an area of concern.

- Fluid loss to the target zone. Here again, a bactericide will be carried into a zone by water or mud lost to the zone. When the zone is tested, or completed and produced, at least part of the biocide may return with produced fluids. Such treated water should be either diluted with other produced fluids or contained with mud for subsequent disposal.
- Injection into a formation during fracing. To prevent innoculating a formation with SRB, frac fluids are sometimes sterilized with bactericides. This water will return when the well is produced, bringing back some of the bactericide. This water must be handled properly to avoid dumping chemical into the environment. Directing this water through a water disposal system is an acceptable alternative to dumping.
- Disposal of mud and packer fluids. Suitable practices must be worked out to dispose of such fluids from each drill site. Because many other chemicals are also present in muds and packer fluids, bactericides are only a part of this problem.
- Spills. The accidental upset is always a danger in any operation. Properly designed SPCC plans for emergency actions to be taken in the event of a spill will minimize contamination from this source.

Mechanisms for Removal

In the event that some bactericide-treated water does escape to the environment, certain natural forces will eventually reduce the hazards.

- Dilution by produced or receiving waters. Bactericides are lethal only above certain concentrations. Dilution by other produced water and/or receiving water will reduce concentrations to below hazardous levels.

- Absorption on clay and soil. Cationic bactericides such as quaternary amines and other amines are readily adsorbed onto clays and similar active surfaces. Anionic bactericides may also be adsorbed by some soil particulates. In such form, the bactericidal function is inhibited. Therefore, bactericide in solution which is spilled onto the ground may be leached from water by adsorption, reducing the hazards to fish and aquatic life.

- Incorporation into benthic deposits. In streams and water bodies there is a natural flocculation and precipitation process which acts as a natural water purifier. This process can adsorb dissolved surface active materials such as bactericides. In so doing, the solids carry the adsorbed chemicals to the bottom to become part of the bottom sediments.

- Biological decomposition. Although a bactericide in use concentration is lethal to microorganisms, bacteria can and will utilize the chemical once it is diluted below lethal concentration. This method of removal is dependent upon sufficient dilution. But it will take place whether the chemical is dissolved in water or adsorbed on clay or bottom sediments in water. Substituted phenols are the most resistant to microbial decomposition, and persist longer if lost into the environment.

- Reactions with other chemicals. Aldehydes and amines in the environment of heavily treated muds may react with other chemicals in the mud to produce a nonlethal chemical product. Although nonlethal, loss of this material is still a pollutant.

- Polymerization at elevated pH. Prior to completion, most muds are often made quite basic with caustic. This high pH will cause polymerization of most aldehyde forms of bactericides and salt out many amine forms. Loss after this occurs will be less hazardous to the environment than loss of the unreacted bactericide.

SUMMARY

Bactericides are often necessary additives to drilling and completion fluids. Like other mud additives, they present a potential hazard to the environment if not used and disposed of properly. Mud disposal is probably the most probable operation through which bactericides may be introduced into the environment. Thus, mud disposal should be carefully designed. Because bactericides must be registered through Environmental Protection Agency procedures, a great deal is known about the effectiveness, treating concentrations, and health and environment hazards of the chemicals. Proper use of these chemicals will reduce the chances of environmental damage through normal usage.

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DISCUSSION

MR. H. H. ZUIDEMA (Shell Oil Company, Houston, Texas): Mr. Robichaux in a table showed an LD_{50} for birds, and LD_{50} is usually expressed in grams or milligrams per kilogram of body weight. Did I understand that this was in grams per gram of total diet?

MR. ROBICHAUX: This is expressed in grams per kilogram of feed for the bird.

There are two ways of determining an LD_{50}. And I was more familiar with your mechanism for determining the concentration of the poison per kilogram of body weight of the deceased bird.

But in recent requirements of the EPA, they want grams per kilogram of food that the bird consumes in a 3-day period.

MR. ZUIDEMA: Three-day period. Thank you.

MR. ROBERT B. ALLRED (Sun Oil Company, Richardson, Texas): Mr. Weir, where did you get your samples? From underneath the shale shaker, as I understood you to say?

MR. WEIR: That is right.

MR. ALLRED: That was hole mud, then?

MR. WEIR: It was hole mud, after the cuttings had been removed. We did not have control over our samples which were supplied by the group that we were working for. They were taken by the operator from the shaker under flow.

MR. ALLRED: That is not representative of what goes into the sea.

MR. WEIR: That is right; we knew that. We have tested other samples; we have done toxic testing on actual discharge materials.

DR. JOSEPH G. MONTALVO (Gulf South Research Institute, Baton Rouge, Louisiana): I would like to address a comment to all three of the panel members. When one presents data on bioassays, one has to be quite careful that the data does include a detailed chemical analysis of the constituents in the sample, if one is doing the bioassay work on a sample such as barite or mud. This detailed list of chemical analyses should include the major constituents, the minor constituents, and

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the trace constituents. I think in the field of pesticide bioassays, it has been established fairly recently that in some instances the measured toxicity was not due to pesticide in the study but was due to the presence in the pesticide of a very minor impurity that had a toxicity far greater than that of the pesticide in the study.

So I think these studies would be more meaningful if we were provided with a list of the chemical constituents in the additives. Thank you.

MR. ROBICHAUX: I agree wholeheartedly.

A lot of times, however, and particularly in the pesticide field, as we find ourselves trying to register pesticides, we are given the ground rules on which to play the game. And so we test the pesticide as such.

Now, along with that, the pesticide branch of the EPA is furnished with a complete list of active and inert ingredients. As a matter of fact, you even have to supply them with your manufacturing process.

So that while we quote here on the basis of generic types, I agree with you that many things need to be said about it. If you are talking about how dangerous a particular pesticide is, then you take it as a whole, as if it were a whole chemical.

MR. CHARLES F. JELINEK (Food and Drug Administration, Washington, D.C.): One thing that all of you in these operations should consider, is the fact that the LD_{50} acute toxicity tests are fine as far as determining damage to certain biota in the environment. But then beyond that, the most important biota to any of us personally is ourselves. We have to consider the fact that fish may only have a few parts per million of some contaminant in them, which will not damage them at all, yet this level in the fish we eat might be quite damaging to us. Therefore, materials such as the chlorinated phenols, which are not biodegraded easily, are those that you should all be particularly careful in handling. If they ever get into streams and become biomagnified in the food chain, you might very well have concentrations that would be toxic to you and me or any other consumer.

DR. STEPHEN P. MURRAY (Louisiana State University, Baton Rouge, Louisiana): As a physical oceanographer interested in currents and dispersion processes, I am having a difficult time relating to the concern about the levels of toxicity for different animals, the shrimp, rainbow trout, and so forth. What do we expect in the environment itself? We don't expect the extremely high concentrations that, I guess, we are having in the lab studies. The natural processes in the sea are extremely rapid around the offshore rigs and I am particularly familiar with that.

If someone could provide a picture of what a mud spill would look like, what would we really be up against in a significant accident on an offshore platform, had a lot of mud turned loose suddenly. Or, are we looking at chronic spillage from the platform? I think Mr. Weir mentioned he might even have some field concentrations; those would be a lot more meaningful to me. What concentrations do we expect in the real environment?

I tend to think that it would be very low, based on my experiences with spray and oil spills.

MR. WEIR: Dennis Wright, a biologist from the Fisheries and Marine Service, Environment Canada, could probably answer that.

MR. DENNIS G. WRIGHT (Environment Canada, Winnipeg, Manitoba, Canada): We have been experimenting with "chironomid" larva--a freshwater insect--and we have been able to show that very thin layers of drilling fluids, one millimeter thick, will cause about a 50 percent decrease in the survival of these insects over about a 3-week period. And I think, judging from some of the studies that we made in the Mackenzie Delta, that these layers are quite probable in the environment.

We looked at one lake where they had a spill of some fluid; we have seen up to about 5 or 6 millimeters of mud on the bottom, and the bottom fauna has been severely reduced in this lake.

MR. CHESSER: May I make a comment to what we have seen offshore?

Lignosulfonate, of course, will impart a brown coloration to the water at a relatively small concentration, and we have observed this over a number of years where water-base fluids have used considerable amounts of the lignosulfonate and where these cuttings have gone into the water. I have never seen any coloration development from the fluid that has been attached to these cuttings, which indicates it would be a relatively small amount at that point.

MR. DANNA W. LARSON (Exxon, Houston, Texas): Tomorrow afternoon Dick Zingula will be addressing this subject, the insight to measurements.

DR. GEORGE R. HOLLIDAY (Shell Oil Co., Houston, Texas): Shell will also be presenting a discussion.

Mr. Weir, I would just ask a question of you to be sure that I understand.

Your values were presented in percentages, I assume, in parts per million and milligrams per liter. We are talking about 90,000 parts per million as your minimum toxicity level; is that correct?

MR. WEIR: Well, what we measured was the hole mud sample. And it is the percentage as it was diluted from 40 liters. Fifty percent was one to one. So it was a percentage of the sample. It was the amount of the dilution of the hole mud, which was not determined in parts per million, no.

DR. HOLLIDAY: So we can relate that to parts per million to get some correlation with that of the other gentleman?

MR. WEIR: Most of the work we have done in the hole muds have been in percentages. We have tried working back, but it doesn't work that well. We have tried to do it on a parts per million basis by individual components, but we have not been able to get reliable data.

DR. HOLLIDAY: Under those conditions, then, would you expect to discharge half an ocean full of mud into the ocean so as to get this pollution? I am having trouble getting the correlation between one to one, if I discharge the mud into a receiving body of water.

MR. WEIR: We were not concerned in our experimentation with receiving water. We were looking at the acute toxicity of the sample to be controlled, not as to its effect on the receiving water or the dilution required to make it nontoxic. We were interested in what was the toxicity characteristic of the mud, per se.

MR. IRVING J. GRUNTFEST (Environmental Protection Agency, Washington, D.C.): While the vendors are here, the question arises of what is the fraction of a particular ingredient (for example, a bactericide) used here of the total national production of that ingredient. Since we are concerned with a domestic problem, is this in any case a substantial or a dominant fraction of the total production of a particular material used in this application? Or is it more typical that the materials that are used here are used in enormously larger quantities in other applications? I address the question particularly to the vendors of the various materials. I think barium sulfate is probably a material that is used to a greater extent here than in other applications I have heard of, but I think bactericides that you have mentioned are probably used in much greater volume in other applications.

MR. ROBICHAUX: Speaking of bactericides, specifically, you are perfectly correct. As a matter of fact, in our own company we have several bactericides and we do not have any registered for use in drilling muds.

That is not true with some of the others who are in the same sort of business we are in. But I feel in the producing operations, in secondary recovery operations, and in saltwater disposal operations, the preponderance of bactericides used in the petroleum industry are used in other than drilling fluids.

As you say, the other chemicals that you find here would probably fit a very wide spectrum because barium sulfate is most heavily used in the drilling fluid business. As to how you would have your chemicals distributed in industrial uses, I think you would find everything from barium sulfate on one extreme to the bactericides on the other.

MR. RICHARD S. SCALAN (University of Texas, Marine Science Institute, Port Aransas, Texas): Mr. Weir, I wonder, since your samples came from below the shale shaker, whether you can eliminate the effects of the materials that might have been picked up from the borehole from your experiments?

MR. WEIR: We did not look at the effects of the formation as to what it is contributing to the toxicity on this sample series, but we have, in other test series, looked at it and tried to see whether or not the actual drill cuttings of the formation were contributing to the toxicity of the samples. I cannot give any information about that. It is still in the draft stage of the report.

MR. WRIGHT: Mr. Chesser, in your bioassays with the brown shrimp, did you do any comparison between feeding and not feeding the organisms during the test?

MR. CHESSER: No. We more or less followed the standard procedure where we did not feed them 3 days prior to the test nor during the test. We have made no variation of the feeding operation.

MR. WRIGHT: I see. It would seem highly probable that in an organism with a high metabolic rate, such as the shrimp, that you could get significant effects by not feeding them; they would probably starve to death during the 7 days of the test.

MR. CHESSER: I don't believe so, because we have a control tank that is not involved in any of the chemicals. We had good mortality rates in that control tank.

MR. WRIGHT: What sort of mortalities were you observing in the control?

MR. CHESSER: For the most part there would be none. In some tests we may have had one.

CHAIRMAN LUMMUS: I will attempt to summarize our session briefly. I think you will agree that we have covered a lot of ground here today in telling you people some of the techniques and methods involved in drilling of an oil and gas well, and a water well, also some of the chemicals used. We don't have all of the answers yet, but at least I'm encouraged that some very substantial research work is going on that's going to enable us in the future to document some of the effects of some of these materials. This should be of considerable help to the EPA in setting reasonable regulations, one which all interested can live with.

22 May 1975

Session II:

ENVIRONMENTAL IMPACT OF CHEMICALS USED IN WELL DRILLING

C. S. Giam, Ph.D.*
Chairman

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*Professor of Chemistry and Oceanography, Chemistry Department, Texas A & M University, College Station, Texas.

INTRODUCTORY REMARKS

C. S. Giam, Ph.D.

I think it is truthful to say that the organizer of this program is quite brave. He is brave in trying to bring together biologists, engineers, chemists, administrators, all under one roof to discuss the topic of environmental impact. To handle such a topic properly will require quantitative data, numbers, not just statements that at high concentrations something happens, at low concentrations something happens. This is not meant to criticize any previous speakers or future speakers but only as a general statement. I think that to isolate a particular event or an episode and say that under these conditions one observes toxicity, or no toxicity, such statements are incomplete (because this episode may not seriously affect the environment as a whole). It is a difficult topic but I am glad that EPA has taken the trouble to organize this difficult conference.

I do not know in detail how the speakers were selected, but in every conference there is just so much time, so there are constraints in selecting speakers.

Those who are officially speaking today will, obviously have a chance to say what they feel about today's topic. But to those of you who are not official speakers, I would suggest that you do contest, that you do agree or disagree with some of the statements made. So I encourage as many of you as possible to really state your case; wherever possible, minimize your emotions, and have as many facts as you can.

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THERMAL DEGRADATION OF DRILLING MUD ADDITIVES

Leroy L. Carney and Dr. Lawrence Harris*

Abstract

Much research effort and expense by service companies and oil companies alike has been devoted to studying the temperature stability of drilling fluids. Even though about 98 percent of the wells drilled have bottom hole temperatures of less than 250° F, fluids must be designed for drilling the wells which encounter temperatures above the 250° F range.

Since the rheology and fluid loss characteristics of drilling fluids are influenced by additives that are primarily organic in nature, their degradation with respect to increased temperature in drilling fluid environments is discussed. Basically, with increases in temperature and pressure many reactions are catalyzed or expedited toward completion. Thus, reactions such as neutralization and hydrolysis are very important in drilling fluid stability.

This paper groups drilling fluid additives into three temperature ranges and discusses their relative temperature stabilities and degradation products. While the common additives used in drilling fluids have been examined for temperature stability, we have selected some of the most widely used additives for examples of how thoroughly these investigations have been carried out.

Because of the complexity involved with many of these reactions, a wide spectrum of analytical tools have been utilized to discern what various degradation products are evolved with respect to incremental increases in temperature.

Thermal degradation of lignosulfonates is discussed as an example of a widely used drilling mud additive.

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INTRODUCTION

A survey of the 1974 Petroleum Engineering literature reveals the following percentages concerning boreholes drilled in the United States as equated to the average bottom hole static temperature encountered.

98.5 percent of boreholes were less than 250° F

1.3 percent of boreholes were greater than 250° F but less than 350° F

0.2 percent of boreholes were greater than 350° F

Therefore, we might say that the majority of the industry's drilling fluids and additives are not subjected to temperatures over 250° F. However, a great portion of the research effort on drilling fluids and related additives is devoted to studies involving temperatures above 250° F. A drilling fluid must be formulated to perform satisfactorily over the total temperature range encountered during the drilling of a particular well. Therefore, it is imperative to ascertain information on the temperature stability of any additive that will be used in a particular drilling fluid system. From a practical aspect, drilling fluids are subjected to elevated temperatures and their performance is observed. These evaluations, while useful for drilling purposes, are empirical in nature but do not relate to actual temperature degradation of the individual components in the system.

DISCUSSION

For this discussion, let us group some commonly used drilling mud additives according to three temperature brackets:

I. Commonly used drilling fluid additives that do not perform satisfactorily above 250° F:
    A. Starches
    B. Guar gum
    C. Xanthanates
    D. Orthophosphate

II. Commonly used drilling fluid additives that perform satisfactorily above temperatures of 250° F, but not above 350° F:

    A. Sodium and calcium lignosulfonates
    B. Tannins
    C. Dual-substituted cellulose derivatives
    D. Polyvinyl acetate/maleic anhydride copolymers
    E. Certain surfactants
    F. Some corrosion inhibitors
    G. Carboxymethyl cellulose
    H. Hydroxyethyl cellulose

III. Additives that are temperature stable above 350° F:
    A. Clay minerals
        1. Bentonites
        2. Attapulgites
    B. Weighting Materials
        1. Barium sulfate
        2. Calcite
        3. Iron carbonate
        4. Iron oxide
        5. Lead sulfide
    C. Salts
        1. NaCl
        2. KCl
        3. Calcium sulfate
        4. Calcium chloride
    D. Bases
        1. Sodium hydroxide
        2. Calcium hydroxide
        3. Potassium hydroxide
    E. Lignites
        1. Mined lignites
        2. Caustisized lignites
        3. Sulfoalkylated lignites
    F. Modified lignosulfonates (organometallic)
    G. Acrylates & acrylamides

H. Most lost-circulation materials

I. Asphaltenes and gilsonites

The materials listed above by temperature groupings are by no means ironclad, since overlapping of some of these materials does occur in regards to temperature functionality. Also to be considered are complexes which form with hydrated bentonite particles. For example, certain bentonite/guar complexes will maintain a rigid gel structure above 400° F.

Since bentonite is the basic ingredient of water-base drilling muds, the interaction of additives with bentonite must be considered in all cases. Due to this interaction, the thermal stability or functionality of organic drilling fluid additives will vary considerably and are determined under the conditions of the drilling fluid system employed.

The thermal stability of cellulose derivatives are especially susceptible to the pH, oxygen content, and metal ion concentrations of the drilling fluid. For example, CMC is more stable to temperature in a pH range of 7 to 9 (ref. 1). The change in characteristics of CMC solutions that may occur during storage or actual use under drilling fluid conditions is usually observed as a decrease in the apparent viscosity of the system.

This viscosity decrease that occurs upon heating to temperatures of 200° F in the absence of oxygen or other oxidizing agents is caused by a decrease in the intramolecular bonding in the CMC polymer that allows the polymer chains to uncoil. This effect is reversible and the viscosity will return as the drilling fluid is cooled.

As the temperature is increased above 250°-300°F, the additional viscosity reduction that results may be caused by scision of the polymer chains, resulting in a decrease in the degree of polymerization (DP). This change is permanent and the viscosity will not return upon cooling.

At these higher temperatures under highly alkaline conditions in the presence of oxygen or other oxidizing agents, oxidative degradation of the cellulose polymer chain occurs (lower DP). The degradation temperature will be considerably lower in the presence of oxidizing agents. Peroxide formation is the primary result of oxygen attack on the polymers (ref. 2). Decomposition of the peroxides can lead to polymers (ref. 2). Decomposition of the peroxides can lead to polymer degradation resulting in permanent loss of viscosity. Wheatham found that at a pH of 12.3, a reducing condition minimized the rate of degradation at 350° F (ref. 3).

The presence of certain trivalent metal cations can extend the temperature limit of some cellulose derivatives by introducing crosslinking in the polymer chains.

Certain other mud additives that we have considered as less temperature-stable (<300° F) are starches, xanthan gums, guars, vinylacetate/maleic anhydride copolymers, and polyphosphates. Guar gums, starches, and xanthan gums can undergo oxidative temperature degradation in the presence of oxidizing agents. Xanthan gums will deacetylate at $pH > 9$ but this affects the system viscosity very little. The presence of small amounts of salts will increase the heat stability of xanthan solutions and trivalent metal cations can crosslink this polymer to increase heat stability. These are just a few examples of some ramifications that can occur in drilling fluid systems.

While empirical data is relied upon for practical applications of drilling fluid, much research effort has been expended behind the scenes, resulting in detailed studies of various drilling fluid additives. Let us look at lignosulfonates as one example. Modified lignosulfonates gained rapid prominence as a very effective dispersant in water-base drilling fluids. They are used successfully at moderately high temperatures, but incremental amounts must continuously be added to maintain effectiveness at higher down-hole temperatures. The greater depths and increasingly higher temperatures of recently drilled oil wells thus indicate a need for determining more precisely the effect of temperature on drilling mud additives.

The complexity of the lignin molecule from which the lignosulfonates are derived, has made quantitative determinations difficult, particularly in drilling mud systems. A study was designed by Skelly &

Kjellstrand (ref. 4) to determine the temperature at which lignosulfonate decomposition begins and the extent to which it proceeds under various conditions. This study was primarily chemical in nature and was not intended to prescribe absolute limits on the use of lignosulfonates under field conditions.

A standard procedure for achieving the aims of the program was developed (ref. 4) utilizing appropriate apparatus; it consisted of the following steps:

1. To 350 ml of a 5 percent bentonite slurry was added 25 g of lignosulfonate dispersant, followed by 233 g of barite, both with thorough mixing. The resulting mud weighed approximately 12 lbs/gal.
2. The slurry was adjusted to pH 10 with sodium hydroxide.
3. The entire mixture was charged to a stirred autoclave equipped with a high-pressure water-cooled reflux condenser and nitrogen inlet valve.
4. The autoclave was pressurized to 400 psig with nitrogen and the apparatus checked for leaks. A valve at the top of the condenser was opened and the apparatus vented to atmospheric pressure and the valve closed.
5. The mud was then heated to the desired temperature with stirring and held at that temperature for 2 hours.
6. The reaction vessel was pressurized to 400 psig with nitrogen. This was done as a practical expedient to prevent flooding of the condenser during the following step.
7. The valve at the top of the condenser was opened slightly to allow the gases to escape at a rate of 9 liters/hour.
8. The vented gases were collected for 2 hours in a scrubber containing 500 ml of standard sodium hydroxide solution while maintaining the desired temperature. The pressure was maintained at 350-400 psig with nitrogen during the venting period.
9. Gas samples (200 microliters) for gas chromatographic analysis were removed from a point in advance of the scrubber

every 20 minutes during the venting period.

10. Carbon dioxide was determined by titrating aliquots of the scrubber solution with standard hydrochloric acid and correcting for acidity due to hydrogen sulfide.
11. Hydrogen sulfide was determined by acidifying aliquots of the scrubber solution and titrating with standard iodine solution to a starch end point.

IDENTIFICATION OF GASEOUS PRODUCTS

The products of the reaction were identified in part by mass spectrometry, gas chromatography, infrared spectroscopy, polarography, chemical analysis and paper chromatography.

Noncondensable gaseous products from the reaction at 410° F were identified as carbon monoxide, carbon dioxide, and hydrogen sulfide. Traces of methyl mercaptan were also present. A mass spectrographic scan from mass 0 to mass 500 showed pertinent peaks at mass numbers 34 (hydrogen sulfide) and 47 (methyl mercaptide radical). These data were obtained by bleeding the gases directly from the reactor into the mass spectrometer. Carbon monoxide was determined qualitatively by means of an M.S.A. carbon monoxide indicator tube. Carbon dioxide was identifed by gas chromatography, utilizing a one foot by one-fourth inch aluminum column packed with silica gel (ref. 5). The concentration of the sulfur-containing gases in most cases was too low to be detectable by this method. Hydrogen sulfide was verified chemically by reaction with lead acetate and with cadmium acetate. A method for differentiating between hydrogen sulfide and methyl mercaptan employing mecuric cyanide and mercuric chloride was used; however, the methyl mercaptan concentration was too low for detection by this method (ref. 6).

DEGRADATION TEMPERATURE STUDIES

A series of tests were carried out in which the temperature was varied from 280° F to 450° F. Results showed that hydrogen sulfide evolution was negligible below 400° F but became significant at 450° F.

Reagent blanks showed that significant quantities of hydrogen sulfide are not emitted at any of these temperatures when lignosulfonates are absent.

The evolution of carbon dioxide in this same series, however, is a better measure of the temperature at which lignosulfonate degradation occurs.

The effect of heating for two 4-hour periods showed that gas evolution began to approach a significant level at about 370° F. At 450° F, the evolution of carbon dioxide became excessive, compared to the potential carbon dioxide possible from the complete degradation of the lignosulfonate. For example, based on an analysis of lignosulfonate for carbon (39.3 percent), hydrogen (4.85 percent), sulfur (5.81 percent) and ash (20.41 percent), the quantity of oxygen (calculated by difference) present in the molecule would prevent the formation of more than 10.0 g of carbon dioxide from the quantity of lignosulfonate used. (This assumes that only a negligible quantity of dissolved oxygen was present since the experiments were conducted in a nitrogen atmosphere.) Based on this figure, it was shown that 21 percent of the potential carbon dioxide can be collected after two 4-hour heating periods at 450° F. This does not include additional decomposition, as evidenced by the formation of carbon monoxide that was not measured quantitatively in these experiments.

The rate of carbon dioxide formation was indicated by plotting gas chromatographic peak heights vs. time. This data was somewhat obscure because gaseous products were allowed to collect for 2 hours before venting was started. Therefore, a plot was made using data obtained by starting the venting under 400 psig of nitrogen as soon as the desired temperature was reached. Heat-up time is still a factor; but, as would be expected, the magnitude of the peaks becomes higher and the slope of the curves becomes steeper as the temperature inceases. At 450° F, the plot does not give a straight line. During the first hour, the decline in apparent reaction rate is quite rapid. During the final 3 hours, however, the rate of decline is much slower, particularly when compared to the slopes obtained at lower tempratures.

The effect of removing some of the mud components from the system was studied. A change in the pattern of gas evolution was noted when barite was removed from the system. In the absence of barite, a noticeable increase in the evolution of hydrogen sulfide occurred at 410° F. This effect was even more apparent at 450° F. The increase in produced hydrogen sulfide was accompanied by a slight decrease in the quantity of carbon dioxide evolved. In view of this, the study of gas evolution from lignosulfonates at lower temperature, 280° F-370° F, was repeated without barite.

It was interesting to note that the "barite effect" was not seen at temperatures of 370° F and lower.

The final pH of the muds (6.0-7.6) after heating 4 hours was lower than in previous tests in which barite was present. With barite present, the final pH was normally 8.0-8.2.

ANALYSIS OF RESIDUAL PRODUCTS

The study of the nonvolatile residual components of the reaction mixture presents a more difficult analytical problem than a study of the gaseous products. For example, literally hundreds of organic compounds are possible from the degradation of lignosulfonates and an absolute identification of all such products formed would be impractical and of little importance with respect to drilling muds. Some brief studies were made, however, to learn something of the nature and type of residual products that form during thermal treatment of lignosulfonates.

Paper chromatographic analyses were made on filtrates obtained after heating lignosulfonate solutions at 410° F and 450° F. The formation of at least two phenolic type products (Rf. 0.14 and Rf. 0.91), not originally present in the reaction mixture, was detected. In addition, one compound found in the unheated reaction mixture (Rf. 0.27) was present in a greater quantity after heating. The chromatograms were developed in a 4:1:1 butanol:acetic acid:water system and sprayed with a 0.5 percent alcoholic solution of 2,6-dichloro-1,4-quinone-4-chlorimide (ref. 7). As a matter of interest, vanillin and isoeugenol, two of the more common products derived from lignin, were chromatographed in the same solvent system giving Rf's of 0.91 and 0.94. Odors reminiscent of these compounds were detectable in filtrates heated at 410° F and 450° F.

Another approach involved analysis of the liquid and solid phases of the residual products for total carbon. After removal of the gaseous decomposition products, the residue was thoroughly stirred and an aliquot was pressure filtered exhaustively until the filter cakes were essentially dry. The filter cakes were analyzed for total carbon by the standard carbon hydrogen method. The filtrates were analyzed for carbon by a modified Van Slyke carbon dioxide method. The carbon content of the filter cakes was higher after heating at 450°F than after heating at 280°F and 410°F indicating insolubilization of the lignosulfonate products, probably by polymerization and/or carbonization.

Further clues as to the distribution of the organic phases of the mixture can be obtained by analysis of the filter cakes and filtrates for sulfur (assuming that complete cleavage of the sulfonate group has not occurred).

It had been hoped that iron and chromium analyses would be helpful in determining the distribution of organic matter between the filter cake and the filtrate. Initially, the chromium is present as a lignosulfonate complex that is completely soluble in water at pH 10.

In the presence of bentonite and barite, however, chromium is essentially completely retained on the filter cake both before and after heating. The small quantities of chromium noted in the filtrates before heating are reduced even further after heating. This was indicated by polarographic analysis to be in a complexed form. No evidence of soluble noncomplexed chromium was noted in any of the tests.

An interesting facet of the data was that most of the chromium is retained on the relatively small quantity of solids formed during heating of aqueous solutions of ferrochrome lignosulfonates at 410°F and 450°F. Similarly, iron was also found to be concentrated primarily on the filter cake.

Some conclusions drawn from this investigation by Skelly and Kjellstrand were:

1. The major gaseous product liberated during lignosulfonate

degradation was carbon dioxide. Hydrogen sulfide and carbon monoxide were formed in lesser quantities. Traces of methyl mercaptan were also present.

2. Under the stated conditions, lignosulfonate degradation begins at about 330°F and progresses continuously until serious decomposition is noted at 450°F.
3. In weighted mud systems, the evolution of hydrogen sulfide is negligible at temperatures below 410°F.
4. As would be expected, the rate of gas evolution becomes increasingly more rapid as the temperature increases.
5. Removal of barite from the system changes the pattern of gas evolution, particularly with respect to hydrogen sulfide evolution at high temperatures.
6. Phenolic type compounds are formed during the reaction.
7. Part of the organic phase of the reaction mixture is insolubilized after heating.
8. The complexed iron and chromium of the ferrochrome lignosulfonate are retained on the filter cake both before and after heating of lignosulfonate-based muds.

From the empirical data of mud rheology versus temperature and a detailed chemical study of thermal degradation of lignosulfonates, it has been concluded that lignosulfonates definitely temperature degrade. Because of this definite temperature degradation of lignosulfonates in drilling fluids and its importance by the function of the fluids, a method was devised by Carney, Skelly, and Gullickson (ref. 8) to determine the quantity of undegradated lignosulfonates in drilling the quantity of undegradated lignosulfonates in drilling fluid systems.

The first step of the method basically consists of suspending a small sample of the drilling fluid in water; one milliliter is usually sufficient. Ammonium acetate is added to the dilute water suspension in order to buffer the solution and to flocculate the clay minerals that are present. The suspension is then centrifuged until the clay minerals and other solids are separated from the lignosulfonates.

The supernatant solution is examined by ultraviolet absorption, and the optical density difference due to the 281 nm peak is determined (figures 1 and 2). This difference can then be related to the concentration of lignosulfonate present in the original sample.

The following general procedure is applicable to most water-base drilling muds containing modified lignosulfonates:

1. Pipette 1 ml of mud from a well-stirred suspension.
2. Dilute with water to 200 ml, add 5 ml of 1N ammonium acetate and dilute with water to 250 ml (higher and lower dilutions may be used, depending on the concentration of lignosulfonate in the mud).
3. Centrifuge aliquots of the well-mixed suspension at 13,000 rpm for 10 to 15 minutes.
4. Place a portion of the clear supernatant solution in a 10 mm silica cell. Scan and record the spectrum from 320 to 240 nm. Any scanning instrument capable of operating from the 500 to 240 nm wavelengths is suitable. (Beckman DBG and DBGT instruments were used.)
5. From the chart, measure the difference in optical density due to the 281 nm peak. Determine the lignosulfonate concentration by reference to an appropriate standard curve.

By using the ultraviolet absorption spectrum and the absorption maximum of lignosulfonates at about 281 nanometers, the following conclusions were ascertained using the optical density difference as related to the presence of lignosulfonate.

1. The concentration level of lignosulfonate in a water-base drilling fluid can be determined.
2. The relationship between the optical density difference obtained by ultraviolet absorption and analysis, and rheology, can be used as a reference point to maintain the optimum treatment level for lignosulfonates in drilling mud.

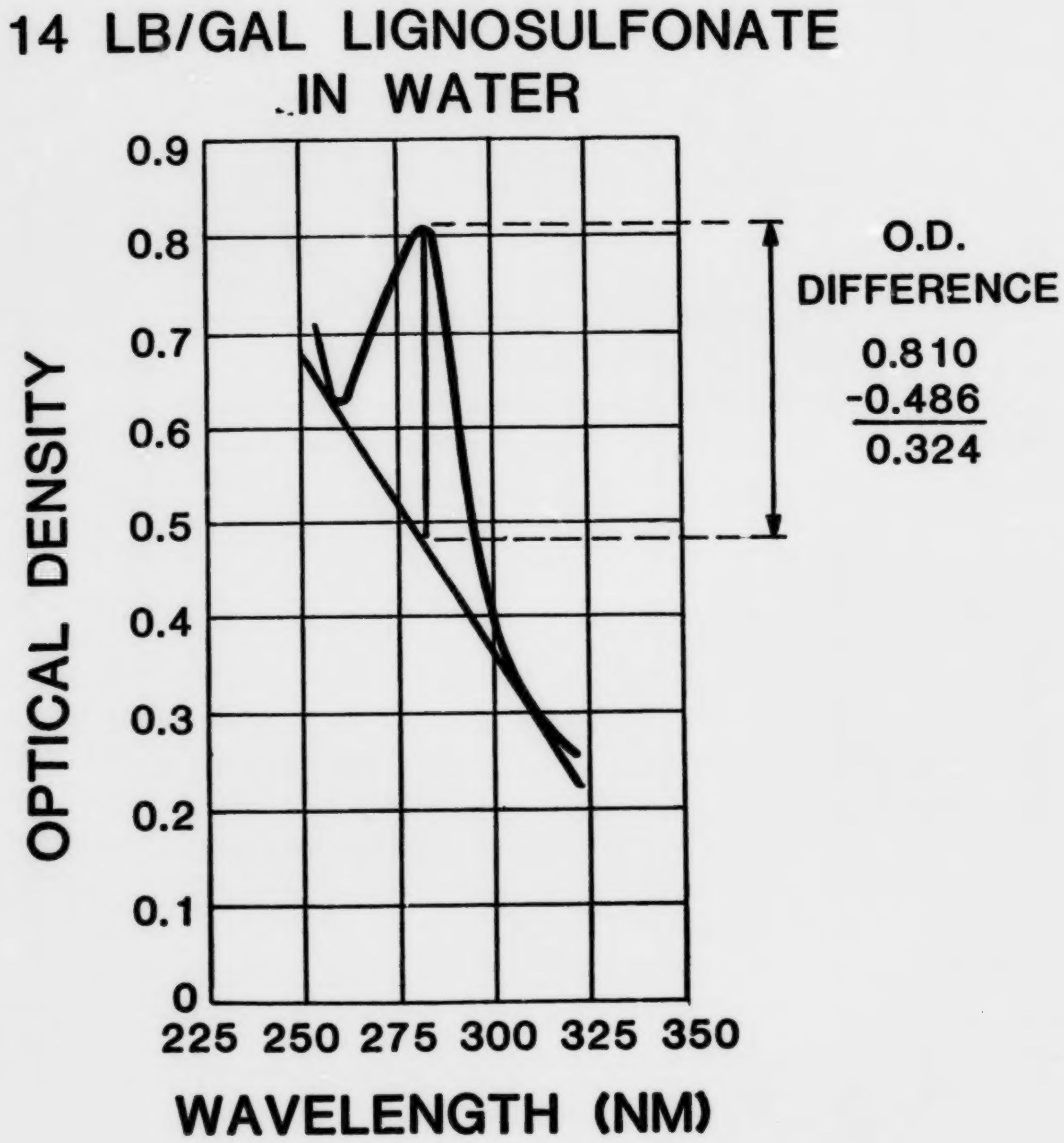

Figure 1. UV absorption maxima of lignosulfonate.

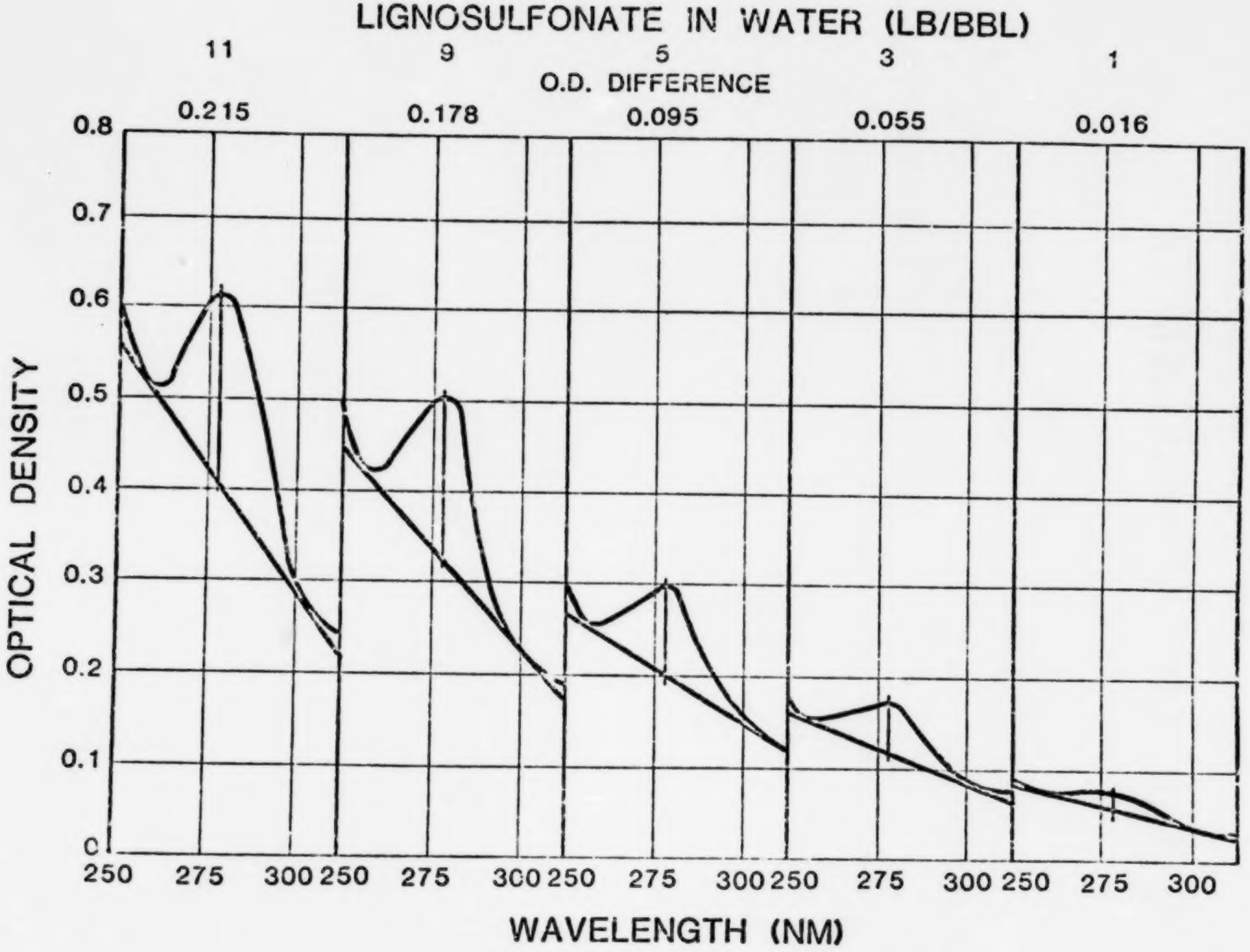

Figure 2. UV absorption maxima of lignosulfonate at various concentrations.

3. The lignosulfonate content of the treating chemical can be monitored to insure product quality of the material on location.
4. The effects of high temperatures in a mud system can be determined and remedial action taken.
5. Various points in a mud system can be monitored. For example, the amount of lignosulfonate present in a fluid before and after centrifugation can be determined and a material balance made.
6. The quantity of lignosulfonate left on solids retained on shaker screens can be estimated and the quantity in the mud passing the screens determined.
7. Mud filtrates can be analyzed to show a relationship between total lignosulfonate contained in the system and the amount of lignosulfonate that will pass through the filter cake and be carried by the filtrate.

In conclusion of this paper, we would like to point out once again that temperature stability of drilling fluid systems are under continual research study in many laboratories and temperatures above 700°F are currently under investigation.

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DISCUSSION

DR. VLADIMIR ZITKO (Environment Canada, Winnipeg, Manitoba, Canada): Did you find any difference in stability between the lignosulfonates from the sulfite process and lignosulfonates from the kraft process? I understand both are used.

MR. CARNEY: There would be quite a difference. Lignosulfonates from the sulfite process, where we normally use what is called a "bisulfite," cook, where your wood chips up to that point are treated the same as in the kraft process; however, here they are put in a digestor. In the digestor is put freshly prepared bilsulfite cooking liquor. This can either be calcium, sodium, or ammonium bisulfite. Under temperature, pressure, and long cooking, this sulfonates the alpha carbon atom on a phenylpropane chain of the benzene range. This deams the lignin, which up to that point is used as a binding agent, water soluble, over the entire pH range.

As a matter of fact, the pH, when it comes out of the digestor, is about 1. This is taken, then, into multieffect vaporators and evaporated up to about 50 percent solids. It can then go various ways. It can be desugared; it can be stripped of the loosely occluded sulfur dioxide, and so on.

The kraft lignin, even though you take the chips like the bisulfite process, is quite a different process in that you are dealing with high alkalinity. You are getting back to what we used to do in drilling fluids by using quebracho extracts, and this type of thing, where we mixed these with caustic soda, taking advantage of the alkalinity for solubility. Therefore, those muds could not run at lower pH's; you would have a pH of 12.5 or higher. So your kraft cook is a very high pH cook, but by taking advantage of this you then separate the lignin from the cellulose. If you reduce the pH of your kraft lignin, commonly called black liquors, you would drop out the lignin as totally water insoluble. Now, you could use this as a source of lignin and sulfonate this through conventional sulfonation reactions, but you're adding onto the cost here because you are already making a separation; then you have a subsequent sulfonation, which would run the cost of the sulfonated kraft lignin fairly high.

Some of this may be used, but I would say probably in limited quantities in relationship to the bisulfite process sulfite liquor.

You would have a purer lignin, from the kraft process and you could actually change your degree of sulfonation. This makes it useful as wetting agents, which are partially soluble materials that can be used and made into combination weighting agents and dispersants. But I would say that the kraft lignin has a very limited use as drilling fluid dispersants.

CHAIRMAN GIAM: I notice from your slide, that high-temperature drilling conditions are at a very low percentage. In the near future would you expect more wells with high temperatures?

MR. CARNEY: Well, this is a pretty difficult question to answer because you have some experts who study the decomposition of hydrocarbons that truly do not think you will find hydrocarbons at the greater depths and temperatures. You have others that think that you will.

We have, as mentioned yesterday, two wells that were drilled in Western Oklahoma--one to 29,500 feet and one to 30,441 feet. These were completed upper hole at about 14,000 to 15,000 feet with some gas show. There was no commercial productivity at those depths where the temperature was 450° to 470°.

CHAIRMAN GIAM: I would like to pose this question to those of you who are dealing with drilling muds at high temperature. If, indeed, you do have pentachlorophenol in your system, say two molecules of it, and if, indeed, you do have sodium hydroxide, and if, indeed, you do have high temperatures, I would imagine that a cylindrical drilling hole would resemble a beaker or flask (chemical reaction vessel), perhaps--and I use the word perhaps--to carry out a condensation reaction (that is, pentachlorophenal condenses to the highly toxic octachlorodibenzo dioxin). Under certain conditions, pentachlorophenol, with a base at high temperatures, will, on paper, anyway--and this statement has to be verified--condense to give you a compound called dioxin. If, indeed, it gives dioxin, dioxin is one of the most potent toxins.

Before I go on further maybe I could ask Dr. Zitko. Are these conditions likely to give dioxin?

DR. ZITKO: Yes. I think these conditions are likely to give dioxin. But I do not think anybody looked: it has not been determined whether it actually happens.

MR. CARNEY: Well, let me say this. You may take some of these things in the laboratory and you may put them in the autoclaves and react them, and certainly you would form some of these reactions because temperature and pressure normally are catalysts for various reactions.

However, as I pointed out before, if you had a well in which the bottom temperature was going to be 400 degrees, I do not think you would sell any operator on a starch mud. Therefore, fortunately, when we have drilling fluid programs designed for high temperature, we normally would not have these materials present. So they do not have an opportunity under these extreme downhole conditions to get together.

Certainly, we do use caustic. Certainly, as temperature increases the reactivity of the caustic increases.

But, normally, we would not have a material like this in a hot mud.

DR. PAT M. WENNEKENS (Alaska Department of Fish and Game, Anchorage, Alaska): There is one aspect I would like to inquire about concerning physical chemical processes. As you go deeper and deeper you are going to go into some hyperbaric conditions in which the pressure effects are also going to influence your reactions. And I would like to get into perspective, essentially, what the effects of both pressure and temperature are going to play in your evaluation of your chemical reactions.

MR. CARNEY: That is a very good question. These things are under continuous study. Once again, it is quite expensive, because the equipment that we must use to reach high pressure and high temperatures in these reactions is quite expensive.

We have autoclaves that we are now studying drilling fluids at 700 degrees and 50,000 pounds of pressure. These little jewels are quite expensive, and one or two runs on those runs into a lot of research money. But pressure is certainly being considered as is temperature.

Now, I emphasized temperature here today because that was the topic of this paper. But along with the temperature we also include the pressure. So, just as in cementing schedules, we run certain casing schedules; we run the temperature and the pressure that would accompany that.

Certainly this does have effects, we find, and we have to sometimes be the leaders in the field, in studying pressure effects on solubilities. Regarding hydrogen sulfide for example that we sometimes are concerned with, we cannot find in the literature, even solubility in various media at high temperatures and pressures. We have the proper equipment and have actually injected hydrogen sulfide in all of its forms at 400 degrees Fahrenheit and 20,000 pounds of pressure and studied the reaction mechanisms and the end products, and the solubilities. Sometimes it becomes important where you would have a greater solubility under pressure, and if you bring materials uphole and the pressure is released, then you may have gases flash off because you have supersaturated the solution due to the pressure.

GROUND-WATER PROBLEMS ASSOCIATED WITH WELL-DRILLING ADDITIVES

D. Craig Shew, Ph.D., and Jack W. Keeley*

Abstract

The importance of ground water is discussed along with the consequences of its degradation. The subsurface environment as a receptor of pollution is discussed in terms of its biological, chemical, and physical characteristics. Suggestions are made as to the technology required for preventing ground-water contamination.

Since many of the topics covered in this session--including the degradation, contamination potential, movement, and toxicity of well-drilling chemicals--deal directly with the ground-water problems associated with these chemicals, and since it would be presumptuous to attempt to compete with experts in these areas, I think it would be of greater value to discuss the subsurface environment as a receptor of these materials and then perhaps to pose a challenge to those whose profession brings them to the exploration of oil, gas, water, and our natural resources.

It is, indeed, gratifying that this conference is even considering ground water as a part of the environment. Not too many years ago, our subsurface water resources were not given consideration in forums such as this and were not even mentioned in polite society. It has only been recently that scientists have begun to appreciate the vastness of ground water and have begun to consider the consequences of its destruction.

It is surprising to realize that while 95 percent of this country's freshwater lies below the surface of the earth, most of our laws, resource planning, research, and academic training deal primarily with

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surface waters. Consequently, when we are done with these activities, our money is spent, and our human resources have gone on to other things, we will have addressed something less than 5 percent of our water problems.

It is not surprising that ground water has been neglected by just about everybody. You cannot swim or fish in it or go on midnight strolls along its shores. Even our august courts have held ground water in awe. Allow me to read a decision from the early part of this century in which the courts passed judgment on this vast resource which accounts for over 95 percent of our freshwater:

> The laws of its existence and progress cannot be known or regulated. It rises to great heights and moves collaterally by influence beyond our apprehension. These influences are so secret, changeable, and uncontrollable, we cannot subject them to the regulation of law, nor build upon them a system of rules. Because the existence, origin, movement, and course of such waters, and the causes which govern and direct their movement are so secret, mysterious, occult, and concealed, an attempt to administer any set of legal rules in respect to them would be, therefore, practically impossible.

In keeping with tradition, in 1971 the Senate Public Works Committee on the Federal Water Pollution Control Act Amendments stated that because "the jurisdiction regarding groundwater is so complex and varied from State-to-State" EPA was not being given authority to set standards in this area. So, we can see that the importance and, indeed, the existence of ground water has been an extremely difficult thing to grasp. We find that the implications of its destruction are exponentially more difficult to deal with. This is due principally to the lethargic nature of the movement of ground water and the more subtle movement of pollutants through either the saturated or unsaturated subsurface environment. The retention time of pollutants in this environment is commonly measured in decades or centuries as opposed to air where it is measured in hours or in reservoirs where pollutants remain for a matter of months. The obvious conclusion then becomes that we simply cannot allow this underground water resource to become polluted and lost because it cannot economically be recovered.

We all know that the nitrate ion is highly soluble. There are reports, however, that indicate that under the influences of rainfall and evaporation, the nitrate ion may take from 8 to 50 years to move only 30 meters downward in alluvial material. It is a reasonable assumption that some organic compounds and their degradation products or metals would move at a considerably slower rate. We can draw the reasonable conclusion that ground water could be monitored for many years near a suspected source of pollution and be declared safe while in fact pollutants are surely and inevitably moving to or through the aquifer.

As a receptor of pollution, the subsurface is an extremely complex environment which changes dramatically in only short distances--vertically or horizontally. A pollutant entering a medium-textured soil would find an extremely large available surface area over which it must pass. For example, the surface area 10 feet below and 5 feet on either side of a septic tank lateral 50 feet long would be roughly equal to the wetted surface of the Mississippi River from its confluence with the Ohio to the Gulf of Mexico. In traversing an area of this magnitude, the chances are good that a pollutant will undergo physical, chemical, or biological alteration.

Biological activity is certainly of prime interest in the movement and fate of pollutants in this subsurface world. Almost all of the knowledge we have in this area is confined to the topmost layers of the earth's crust known as the true soil zone. We know that in this area an intense biological community exists which is biochemically diverse and multitudinous. It is an area where biological climate can change from aerobic to anaerobic within small distances dependent upon the nature of the waste, the availability of moisture, and the potential for aeration.

We are aware that aerobic bacteria are principally responsible for waste stabilization in conventional treatment facilities. We have found that anaerobic bacteria can also play an important role in the degradation of those pollutants which are considered to be stable. DDT, for example, has been found to degrade rather rapidly in an anaerobic subsurface environment. NTA, the proposed substitute for phosphates in detergents, was found to degrade anaerobically. We find ourselves interested not only in the parent compound but its degradation products which may even be more toxic or more soluble than the parent compounds.

The movement of bacteria and viruses is proportional to the size of the voids available for their passage. Where bacteria generally measure a few microns in size, viruses are smaller by roughly two orders of magnitude. The nature of the subsurface then becomes paramount where highly fractured formations will allow passage for considerable distances, while consolidated sands, for example, will prove quite limiting.

Of course, if we are to consider the subsurface biological community in terms of its capacity to degrade pollutants with which it comes into contact or the contamination problems that biological life may cause, we must also consider viability in addition to the ability to move through the subsurface environment. Subsurface water generally experiences an increase in salinity with depth. Surprisingly, however, we can find highly mineralized water at very shallow depths while relatively fresh water can occasionally be found in rather deep formations. Although the availability of water to microbes is limited with increased osmotic pressure, many species of bacteria grow in highly mineralized water, even up to 30 percent salt.

Temperature is one of the most important and limiting factors to the survival of microorganisms, although the effects of pressure, acidity, and other parameters cannot be disregarded. Generally, optimum growth for predominant species ranges between 25° and 40°C with the ultimate temperature for survival being 80° to 100°C. In the upper layer of the earth's crust, biological activity is a direct function of seasonal temperatures; while at increased depths, temperature fluctuations are reduced. Temperatures increase generally at about 30°C for every 1,000 meters of depth. At this rate of increase, most biological activity would be prevented at about 1,800 meters (5,900 feet) and would virtually cease below 2,500 meters (8,200 feet).

Hydrostatic pressures increase at about 0.1 atmosphere for every meter of depth, or something less than 0.5 psi per foot. We know that there are many exceptions to this rule of thumb, but the point remains that pressure increases with depth. Generally, microbes are capable of growing at 200-300 atmospheres provided other factors are acceptable. Although some biological activity has been reported above this pressure, it would seem that the increase in temperature would be limiting before the increase in pressure.

In order for biological activity to occur, there are several conditions which must be satisfied. Carbon in the form of carbon dioxide or organic matter along with lesser quantities of nitrogen, phosphorus, and sulfur in either organic or inorganic form must be present for the synthesis of protoplasm. The subsurface offers a plentiful source of carbon, principally in the form of carbonates; but, appreciable amounts exist as organic matter incorporated into sedimentary deposits at the time of their formation. Although much of this carbon is in petroleum deposits, even greater amounts are present in a finely disseminated bitumen.

Nitrogen, phosphorus, and sulfur are probably available in the subsurface as organic or mineral matter. Like carbon, these nutrients are required for all biological life, but in lesser amounts. It would not seem likely that they would limit such activity. The possibility remains high, however, that limited availability of one or more of these elements will restrict the level of microbial activity.

The availability of molecular oxygen is pretty well confined to the upper layer of the earth's crust where replenishment can occur by gas interchange. Even here, its presence is a function of the rate of gas exchange and the utilization of microorganisms. Although this area is not often important in drilling for oil or gas, it is critically important when dealing with water table aquifers where pollutants must pass through it during the percolation of recharge water.

Since deeper formations are far removed from the zone of aeration and the movement of water and the rate of recharge is near zero, it is not likely that appreciable oxygen or other easily reduced matter could be present. However, the electron acceptors for truly anaerobic organisms are probably present in large quantities at these low depths. The availability of electron acceptors is limiting in the sense that they are replenished at a very slow rate which would account for low biological activity allowing the survival of organic matter, particularly petroleum, over long geological times.

The existing state of knowledge is not advanced enough to allow more than speculation on how long microorganisms have been in some of these deeper formations. It is complicated because those organisms do not differ from those found at the surface. Those found in deep formations may have been deposited with the sediments millions of years ago, or they may have migrated there over very long times. Many do have the capacity to propel themselves either to reach better living conditions or to escape a more hostile environment.

The overriding point is that while drilling we pass through formations which permit the existence and activity of biological life. The community has obviously been in a rather delicate balance for very long periods of time. While drilling we introduce, at least locally, additives which disturb this ancient biological balance, and it is the consequence of this disruption that is of importance to us at this gathering. The significance of such a disturbance to ground-water pollution and pollution control resides in the potential interactions of the microorganisms and pollutants introduced and these interactions on the quality and availability of ground water.

Conceptually, we would consider that altering an existing biological community would be beneficial in that organics can be eliminated and nitrates reduced by denitrification. There is also some evidence that the metabolic products of degradation of some drilling additives might be less desirable than the parent compounds either from the standpoint of toxicity or in the reduction of permeability.

At this point, I think some of our experience in subsurface research is pertinent. We have found, for example, that DDT which was considered biologically stable is in fact degraded in the subsurface environment. We know that DDT has been considered particularly toxic to man. In ground water, DDT does not migrate to any great extent due to its low solubility and high affinity for formation material. The important question then concerns the nature and solubility of the anaerobic degradation products. If they become free to move through the aquifer and are more toxic than the parent compound, our microbes have behaved in a detrimental manner.

Not long ago a compound called NTA (nitrilotriacetic acid) was suggested as a substitute for phosphates in detergents. The substitution was suggested as a means to reduce one of the nutrients believed to be a major cause of eutrophication in surface waters. It was feared, however, that the degradation products, resulting from conventional aerobic waste treatment, might cause cancer. To that point, the scientific community was convinced that the compound was anaerobically stable. We became concerned because millions of septic tanks in the country treat waste anaerobically and, as pointed out earlier, we often find anaerobic conditions in shallow surface soils.

We found that NTA was indeed degraded in simulated anaerobic ground-water conditions by bacteria actually taken from shallow aquifer sands. In this case, however, it appears that the bacteria are working for us in that the end products of degradation are harmless and that intermediate products are short lived.

Those of us interested in ground-water resources find ourselves in a rather pathetic position. For years we have tried to get resource planners to consider this abundant water supply. We have tried to get everyone to appreciate the importance of preventing ground-water pollution from the standpoint of the long residence times involved. The Safe Drinking Water Act which was passed last December provided for the first time legislation which covered ground water, and suddenly everybody is asking questions for which we simply do not have answers. Research concerning the underground environment is lagging behind that of surface water and waste treatment by many years.

Basic to the understanding of the fate of any pollutant in this underground world is the understanding of that world as a receptor of pollution. It is a very complex world and a very variable world in which simply measuring its components is difficult.

How can we be sure that samples taken to identify the biological community are not contaminated by drilling? How can we be expected to measure the oxidation-reduction potential below the surface of the earth without altering it during sampling? What means could be made available to determine the amount and composition of gases at great depths?

Obviously, those of you who have spent your lives drilling for oil, gas, water, and other resources are best equipped to develop drilling techniques which will allow us to answer these questions. In the past you have had to develop unique techniques to answer your own particular needs. I am suggesting that a problem is before you again in that the protection of our tremendous ground-water reserves is as important to our future needs as any problem you have faced in the past.

CHEMICAL APPLICATIONS IN OIL- AND GAS-WELL-DRILLING AND COMPLETION OPERATIONS

A. Gene Collins*

Abstract

An investigation was made of the chemicals used and their applications in oil- and gas-well-drilling operations as they may affect ground waters. The study indicated that some of the constituents used in oil-base muds or drilling fluids, water-base muds, and well-completion additives, if improperly handled or in the event of an accident, could contaminate ground waters. Chemicals are used in these drilling muds and well-completion additives to control bacteria, calcium, corrosion, density, dispersion, emulsion, foam, filtrate reduction, flocculation, heavy shale, lost circulation, lubrication, pH, surface activity, and viscosity. Although contamination of potable ground waters by drilling operations is possible, experience has shown this to be the exception rather than the rule.

INTRODUCTION

In 1833, Fauvelle (ref. 1) in France observed that drill bit cuttings were brought to the surface by the flow of water during an artesian well-drilling operation. M. T. Chapman in 1890 obtained a patent on a rotary-well-drilling method concerned with circulation and recirculation of water containing clay particles generated in the well bore. These are some of the earliest recorded uses of drilling fluids.

In addition to the removal of drill cuttings, it became apparent that drilling fluids (muds) were useful in increasing wall support of the hole, sealing permeable formations for exclusion of high-pressure gas and water, and preventing gas blowouts and lost circulation. Drillers recognized a relationship of the colloidal properties of the different types of clays to water loss, lubrication and cooling of the bit and drill pipe, and gelling tendencies of clay fluids. The drillers began to prefer certain types of clays, and it was soon recognized that drilling fluids containing clays had a disadvantage because they tended to seal off oil- and gas-bearing formations, necessitating the removal of the clay sheaths from producing formations.

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Because clay in a water-base drilling fluid has the tendency to seal thoroughly an oil- and gas-bearing formation, some drillers use oil-base or oil-emulsion drilling fluids, especially in well-completion operations. Water-base fluids also have the detrimental tendency of causing the reservoir rock to become water-wet, forming a "water block" that adversely affects the flow of oil into a well. The first major efforts to create oil-base drilling fluids occurred in 1935 (ref. 1).

An opening or cylindrical hole from the ground surface to a subsurface oil- or gas-bearing formation is an oil or gas well. Such an opening usually is lined with a metal pipe cemented in place, and production equipment is fastened to the cased hole to regulate and control oil or gas withdrawal rates. Before drilling a well, some knowledge of the geologic formations to be penetrated is useful, as is knowledge of the approximate depth of the target petroleum-bearing zone. This information is needed so that the appropriate diameter, length, and type of tubular goods can be selected in planning the well.

Most States have and enforce laws requiring the setting of surface casing to protect the fresh-water subsurface sands from invasion by brines and hydrocarbons from deeper horizons. Therefore, a minimum of two strings of casing--the surface casing and the oil-string casing--almost always will be required. Additional strings of casing may be required if heaving shales are found while drilling, if abnormal pressures are encountered, or if a zone of lost circulation is found. Each additional string of casing requires more capital and increases the cost of the well.

If appropriate precautions are not taken in planning, drilling, and completing an oil or gas well, disastrous consequences can occur. For example, during drilling operations or when pulling the drill pipe, a well may blow out if adequate mud pressure is not maintained. Such a situation may develop if the mud line is accidentally broken or if the well casing is not properly cemented to competent zones.

In spite of the numerous possible accidents and potential hazards of drilling and completing wells that intersect brine and fresh water aquifers, little ground water pollution has occurred. This record is to the credit of the petroleum industry because of its constant endeavors to maintain safe nonpolluting working procedures.

USES OF DRILLING FLUIDS

The most modern drilling method is the rotary system which requires a circulation of drilling fluid for removal of drilled cuttings from the bottom of the hole to keep the drill bit and the bottom of the hole clean (figure 1). The drilling fluids are pumped from ground surface through a drill pipe and bit to the bottom of the hole and returned to the surface through the annulus between the hole and the drill pipe. The flow of formation gas, oil, and brine into the drill hole is blocked by the drilling-fluid column which produces a hydrostatic pressure that counterbalances or exceeds the formation pressures.

Drilling fluids or drilling muds are used in well drilling for several reasons. Some of the major functions of drilling fluids and of the constituents in them are to control bacteria, calcium, corrosion, density, dispersion, emulsion, foam, filtrate reduction, flocculation, heaving shale, lost circulation, lubrication, pH, surface activity, and viscosity.

Bactericides are added to reduce and control the bacteria in a drilling fluid. Common bactericides are paraformaldehyde, hydroxides

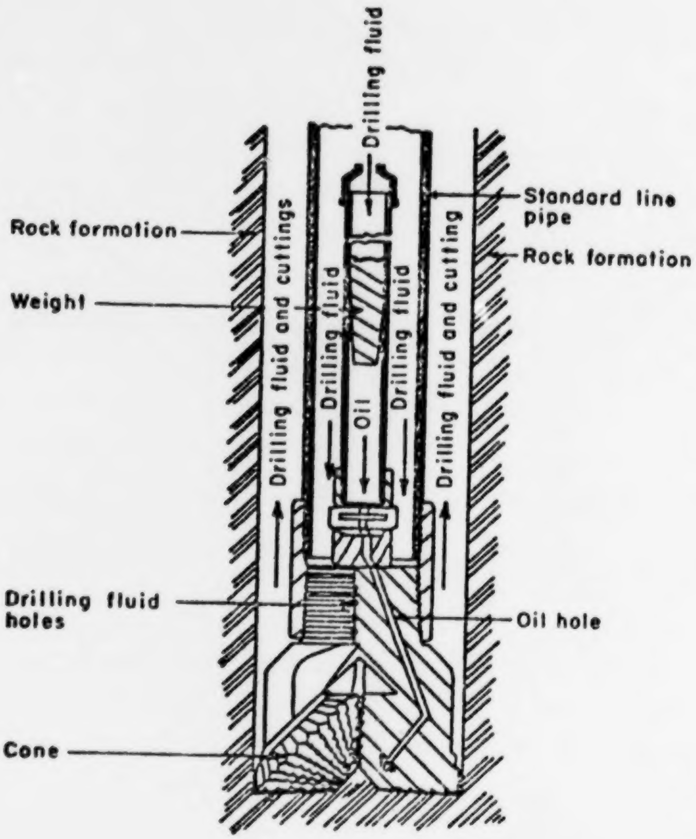
Drilling fluid
Standard line pipe
Rock formation
Rock formation
Weight
Drilling fluid and cuttings
Drilling fluid
Oil
Drilling fluid
Drilling fluid and cutting
Drilling fluid holes
Oil hole
Cone

Figure 1. Schematic of a drill bit illustrating the influent of drilling fluid and effluent of drilling fluid plus drill cuttings.

of sodium or calcium, and sodium pentachlorophenate.

Calcium precipitators are used to remove excess calcium from the drilling fluid. Calcium compounds are solubilized in the drilling fluid when the drill bit is drilling into rocks containing anhydrite or gypsum. The excess calcium compounds destroy the effectiveness of other chemicals in the drilling fluid if they are not removed. Some of the compounds used to remove the excess calcium are sodium hydroxide, sodium carbonate, sodium bicarbonate, and barium carbonate.

Corrosion inhibitors are added to drilling fluids to prevent corrosion of the mud-circulation system: drill pipe, string, and bit. Chemical agents used to control corrosion include water-soluble amines such as high molecular weight imidazoline. Most of the amine inhibitors are marketed under brand names. Copper carbonate and calcium hydroxide are used in some applications as a corrosion inhibitor as are oxygen or sulfide scavengers such as formaldehyde, sodium sulfite, and iron oxide. One high-temperature inhibitor is a combination of sodium arsenite plus alkyl phenolethylene oxide. Most emulsified oil-base muds exhibit excellent corrosion-inhibition properties.

Density controllers are used to control the density or weight of the drilling fluids. High-density fluids are used to control well backup pressures resulting from subsurface formation pressures, facilitate the pulling of drill pipe, control formation caving, and resist loss of circulation.

Higher density fluids are used to counteract formation pressures, which can be very high in abnormally pressured or geopressured zones. The hydrostatic gradient of fresh water is 0.433 psi/ft and of brine containing 80,000 parts per million (ppm) of sodium chloride (NaCl), 0.456 psi/ft, whereas a geopressured zone may be as high as 1.0 psi/ft or equal to the entire geostatic weight of the overburden (ref. 4). In such a situation, a mud weight of 19.3 lb/gal would be necessary to prevent a well from blowing out. In the Gulf Coast area, formation pressure gradients that exceed 0.465 psi/ft (9.0 lb/gal mud density) usually are considered abnormal pressures (ref. 4). Compounds used to increase the density of drilling fluids include barium sulfate, calcium chloride, calcium bromide, calcium carbonate, iron oxide, and lead sulfide.

Dispersants and thinners are chemicals that can change the viscosity and the amount of dissolved and/or suspended solids in the drilling fluid. For example, dispersants can be used to change a gel strength or increase or decrease the mud weight. Deflocculation is a prime purpose of a thinner to minimize association of clay particles. Emulsification is the formation of a substantially permanent heterogeneous mixture of two liquids. Emulsifiers used in formulating drilling fluids are surface-active agents such as soaps, sodium sulfonates, or sodium alkyl sulfates.

Foaming agents are added to drilling fluids to cause foam while drilling in aquifer formations. Such foams permit air or gas drilling through water-bearing formations. The chemical agents used are surface active or surfactants and include organic sodium sulfonates, and alkyl benzene sulfonates both branched-chain and linear-chain. Most of the foaming agents are sold only by brand name.

Defoamers are used to control foaming action that sometimes occurs with salt-water muds. Common defoamers are long-chain alcohols, silicones, and sulfonated oils.

Filtrate reduction in drilling means reducing the amount of drilling fluid that passes into the rock formation being drilled. Chemicals added to the drilling fluid to inhibit loss of fluid to the formation include sodium carboxymethylcellulose, bentonite clay, barium carbonate, oil-base muds, various lignosulfonates, sulfonated asphalt, and pregelatinized starch.

Flocculating or coagulating agents sometimes are used to form a stronger drilling mud gel. Such an agent causes suspended colloidal particles to group together or "floc" and settle out of solution forming a gel precipitate. Chemical agents that are used include clays such as bentonites, aluminum sulfate, calcium sulfate, and ferric sulfate.

Shale-control additives are used to inhibit the swelling and caving of shales caused by hydrous disintegration. Products used to control heaving shales include calcium chloride, calcium sulfate, calcium oxide, calcium lignosulfonate, sodium chloride, sodium silicate, colloidal asphalt, sulfonated asphalt, polyanionic cellulose, gilsonite, aluminum lignosulfonate, and chrome lignite.

Lost-circulation additives are used to plug a zone into which the drilling fluid is being lost, to prevent a complete loss of the drilling fluid into the formation being drilled, and hence a loss of drill fluid circulation from the bottom of the drill hole to the top. Agents used to plug such a zone include inorganic chemical grouts or cements containing mixtures of silicates, metallic oxides, and limestones; organic chemical grouts containing mixtures of acrylic monomers with catalysts; causticized lignites; fibers such as sugar cane, straw, pig hair, cedar fiber, ground nut shells, expanded perlite (volcanic rock); shredded cellophane, ground rubber; mica; carbonates; shredded leather; oil soluble resins; and barite.

Lubricants are added to drilling fluids to reduce the friction coefficient at the drill bit. Common lubricants are graphite, soaps, crude oil emulsions, organic polymers, gilsonite, water-dispersable asphalts, and oil-dispersable asphalts.

The pH, adjusted by the addition of an acid or a base, is adjusted because certain mud or fluid additives often are soluble at a certain pH.

Surfactants or surface-active agents are used in drilling fluids to reduce the interfacial tension between contacting surfaces such as water and rock, or water and oil. Surfactants were discussed under emulsifiers, foamers, defoamers, and flocculators. Therefore, the type of surfactant added to the drilling fluid is dependent upon what surfaces are involved and the kind of reaction desired.

Viscosifiers are constituents added to the drilling fluids to build a high viscosity-dissolved solids interrelationship. Some of the compounds employed as viscosifiers are attapulgite and bentonite clays, quebracho, polymeric lignosulfonate (crude oil emulsifier), long-chain-polymer xanthum gum, calcium magnesium silicate, causticized lignite, sodium tetraphosphate, sodium acid pyrophosphate, sodium hexametaphosphate, organic polysacchoride, and pellitized crysotile asbestos.

Sulfonated drilling muds are prepared by: (1) sulfonating asphaltic crude oil with sulfuric acid, followed by neutralization with sodium silicate and ion exchanging with hydrated lime; or (2) absorbing concentrating sulfuric acid on a porous carrier, e.g., diatomaceous earth, and then sulfonating asphaltic crude oil with acid carrier, followed by partial neutralization with sodium hydroxide and ion exchanging with hydrated lime.

The usual asphaltic crude oils that are used yield a 5- to 7-weight-percent carbon residue and have an API gravity in the range of 26° to 31°. Some blends may contain an 18° API asphaltic crude oil with a 12-weight-percent carbon residue blended with a paraffinic 42° API crude oil with a 0.5-weight-percent carbon residue. These muds are usually mixed with oil at the drilling site and used in the drilling operation. As the cuttings plus the used drilling mud are recovered from the well, the drilling mud is usually separated from the cuttings and reused.

The use of quebracho, starch, and carboxymethylcellulose in formulating drilling muds has decreased in the last decade; whereas, the use of chrome lignosulfonates has increased. The use of lime-treated mud systems has also decreased; whereas the use of low-solid muds, invert emulsions, and chrome lignosulfonate systems has increased.

Chemical Treatment of Completed Wells

Wells are treated with acids to increase the permeability of the reservoir rocks. This increases fluid flow and increases the recovery of oil and gas; it also improves fluid injection in secondary oil-recovery and disposal operations. Hydrochloric, nitric, sulfuric, hydrofluoric, formic, and acetic acids are used. Such treatments produce soluble compounds including calcium chloride, sodium sulfate, sodium fluoride, etc., and in addition, may leave partially spent acids in solution.

The volume of acid used to acidize a well may vary from 500 to several thousand gallons depending upon the amount of acid-soluble strata, the thickness of the horizon being treated, and the calculated productivity of the well (ref. 4). Table 1 lists the approximate amounts of hydrochloric, formic, and acetic acid used in the United States in 1969 for oil- and gas-well treatment.

Corrosion Inhibitors

Table 2 lists the approximate amounts of corrosion inhibitors used in well drilling operations in 1969 (ref. 4).

Table 1. Volume of acids used for oil- and gas-well treatment

Acid	Gal/yr
Hydrochloric	8.7×10^7
Formic	2.0×10^5
Acetic	1.0×10^5

NOTE: gal × 3.785 = liter.

Table 2. Types and amounts of inhibitors used in oil- and gas-well treatment

Inhibitor	lb/yr
Sodium arsenite	1.0×10^6
Imidazoline	1.25×10^6
Abiethylamine	7.0×10^5
Coal tar derivatives	2.5×10^5
Acetylenic alcohol-alkyl pyridine	3.0×10^5

NOTE: lb/yr × 0.454 = kg/yr.

Table 3. Types and amounts of other additives used in oil- and gas-well treatment

Additive	lb/yr
Lactic acid (44 percent)	5.75×10^5
Citric acid	2.0×10^4
Alkylaryl sulfonic acid	5.0×10^5
Zirconium oxychloride (20 percent)	2.5×10^5
Quaternary ammonium derivatives	2.0×10^5
Polyacrylamide	6.0×10^5
Polymers	1.0×10^5
Guar gum	5.75×10^6
Fluid loss agents	1.8×10^6
Emulsion preventers	4.5×10^5

Other Additives

Table 3 lists the approximate amounts used in 1969 of some of the other additives used in drilling fluids.

WATER-BASE AND OIL-BASE SYSTEMS

Drilling fluids usually consist of water-base or oil-base systems. The water in the water-base systems, where water is the continuous phase, can be fresh water, brackish water, saturated salt water, or gypsum-treated water. The pH of these waters will range from about 7 to above 11 (ref. 2).

An oil-base system is a fluid in which oil is the continuous phase and water is the dispersed phase. The system may contain 50 percent water by volume in the liquid phase in invert emulsion muds. Oil used in these systems usually is a mixture of asphalt and diesel fuel. Diesel fuel is used to thin and reduce viscosity, whereas asphalt and clays are used to thicken and increase viscosity.

Oil-base muds (not the invert emulsion type) contain up to 5 percent water, which is emulsified into the system with caustic soda, or quick lime, and an organic acid. Therefore an oil-base mud is differentiated from an invert emulsion mud primarily by the amount of water; yet both types are water-in-oil emulsions (ref. 2).

ESTIMATED COST OF DRILLING FLUIDS

Drilling fluids are expensive; an average cost is about $200 per well per day. Drilling fluids must be continually replenished because of loss of fluid to porous rocks in the hole and to the formation of the wall sheath. If circulation is "lost" in a very permeable or cavernous formation, large amounts of new drilling fluid are used. The volume of drilling fluid in use at any given time during a drilling operation ranges from about 500 to more than 1,500 barrels. Assuming that there are 1,500 drilling rigs in use, the annual drilling fluid cost is about $100 million.

Considerable money is invested in drilling muds, especially in the heavier muds; consequently, they are recovered for reuse. Such muds are primarily used for emergencies, such as lost circulation and high-pressure kicks from both gas and salt water. Many of the used muds are treated with high concentrations of lignosulfonates to produce a stable mud with specific properties.

CONCENTRATIONS OF SOME CONSTITUENTS IN SOME OILFIELD BRINES

Because all types of drilling fluids can be prepared with natural oilfield brines, the constituents found in these brines plus the concentrations of the constituents should be considered. Tables 4, 5, and 6 show the concentrations of some constituents found in oilfield waters in the United States. Table 4 contains an analysis of oilfield waters from Tertiary age sedimentary rocks; table 5, Jurassic age sedimentary rocks; and table 6, Pennsylvanian age sedimentary rocks. The data shown in the tables are the highest values found, the average values, and the number of samples analyzed (ref. 4).

COMPOSITION OF CRUDE OILS

Crude oil sometimes is used in preparing oil-base drilling fluids. The composition of crude oil varies from one geologic reservoir to another. The solubilities of petroleum hydrocarbons in water is small. Aromatics are less than 0.2 percent soluble in water, whereas n-octane and heavier hydrocarbons are less soluble than 1 ppm (ref. 5) at room temperature and pressure. The solubility of n-octane is 11.8 ppm at 149°C, and the solubility of topped crude oil is 20 to 40 ppm at 150°C (ref. 6).

Table 7 illustrates the approximate amounts of paraffin hydrocarbons in some crude oils taken from Tertiary, Jurassic, and Pennsylvanian age sedimentary rocks. The compounds in crude oils that boil above 527°F are removed by vacuum distillation (ref. 7).

Table 4. Tertiary system, highest concentration in mg/l of a constituent found, average concentration, and number of samples analyzed

Constituent, mg/l	Highest	Average	No. of samples
Lithium	27	4	169
Sodium	103,000	39,000	379
Potassium	1,200	220	176
Rubidium	0.6	0.24	11
Cesium	0.4	0.20	9
Calcium	38,800	2,530	376
Magnesium	5,800	530	368
Strontium	420	130	142
Barium	240	60	140
Boron	450	36	170
Copper	1	0.63	3
Chloride	201,300	64,600	380
Bromide	1,300	85	323
Iodide	35	28	322
Bicarbonate	3,600	560	364
Carbonate	300	75	8
Sulfate	8,400	320	139
Organic acid as acetic	1,900	140	53
Ammonium	2,700	230	64

POSSIBLE WAYS DRILLING FLUID MAY CONTAMINATE GROUND WATER

Chemicals used in well-drilling operations could contaminate ground waters in the following manner:

(1) If the conductor casing and/or surface casings shown in figure 2 are not properly cemented to competent subsurface zones below the upper ground-water horizons.

(2) If there is an improperly plugged and abandoned well in

Table 5. Jurassic system, highest concentration in mg/l of a constituent found, average concentration, and number of samples analyzed

Constituent, mg/l	Highest	Average	No. of samples
Lithium	400	10	80
Sodium	120,000	57,300	85
Potassium	900	140	9
Rubidium	0.10	0.10	1
Cesium	0.10	0.10	1
Calcium	56,300	25,800	85
Magnesium	5,200	2,500	84
Strontium	2,080	320	9
Barium	50	10	7
Boron	50	13	9
Chloride	210,000	141,000	85
Bromide	6,000	1,200	80
Iodide	40	16	8
Bicarbonate	2,640	140	72
Sulfate	1,480	210	78
Organic acid as acetic	12	12	1

the area, drilling fluids may escape into a deep porous or cavernous formation, come back up the improperly plugged well, and contaminate a near-surface fresh-water aquifer, as shown in figure 3.

(3) If during drilling operations a high-pressure zone is drilled, inadequate mud weight is used, and the well blows out through the top of the hole, drilling fluids can be spilled on the ground with possible contamination of fresh-water aquifers (see figure 4). The blowout may even relocate the surface and/or conductor casings.

(4) If during drilling operations a deep very porous fresh-water aquifer is penetrated, it is possible that considerable drill-

Table 6. Pennsylvanian system, highest concentration in mg/l of a constituent found, average concentration, and number of samples analyzed

Constituent, mg/l	Highest	Average	No. of samples
Lithium	35	7	45
Sodium	101,000	43,000	951
Potassium	710	170	57
Rubidium	2.30	0.55	25
Cesium	8.50	0.15	19
Calcium	205,000	9,100	950
Magnesium	15,000	1,900	947
Strontium	4,500	600	70
Barium	640	30	41
Boron	70	15	54
Manganese	105	60	2
Chloride	270,000	87,600	950
Bromide	3,900	490	57
Iodide	1,410	210	52
Bicarbonate	1,200	130	897
Carbonate	70	40	2
Sulfate	5,400	430	756
Organic acid as acetic	2,300	430	44
Ammonium	3,300	300	51

ing fluid can escape into the porous zone before it can be sealed (see figure 5).

(5) If a drilling-fluid storage tank or associated lines should rupture and spill fluid on the ground, the fluids can seep into the earth and contaminate ground waters (see figure 6).

(6) If during drilling operations a deep vugular and cavernous fresh-water aquifer is penetrated, it is very likely that large amounts

Table 7. Approximate amounts of paraffin hydrocarbons in some crude oils taken from Tertiary, Jurassic, and Pennsylvanian Age rocks

Boiling point, °F	Hydrocarbon, C numbers	Tertiary, percent	Jurassic, percent	Pennsylvanian, percent
95-122	C_7	--	5.5	2.1
123-167	C_8	--	4.8	2.3
168-212	C_9, C_{10}	6.5	5.6	3.6
213-257	C_{11}, C_{12}	9.0	6.7	4.5
258-302	C_{13}, C_{14}, C_{15}, C_{16}	7.5	7.9	4.8
303-347	C_{17}, C_{18}	6.6	7.5	4.7
348-392	C_{19}, C_{20}, C_{21}	5.4	6.6	4.3
393-438	C_{22}, C_{23}, C_{24}, C_{25}	6.0	5.9	5.0
439-482	C_{26}, C_{28}, C_{29}, C_{30}, C_{31}	5.8	6.0	6.0
483-527	C_{32}, C_{33}, C_{34}	6.3	6.3	7.1

of drilling fluid will escape into the zone before it can be plugged or sealed, as shown in figure 7.

(7) If during drilling operations a high-pressure zone is encountered, it is possible that the well may blow out and pollute an upper fresh-water aquifer with some drilling fluid, as shown in figure 8.

(8) If the chemicals used during well completion operations escape into a fresh-water aquifer because of improper casing or tubing, they may cause contamination.

Most States have and enforce laws which prevent the above types of contamination from occurring.

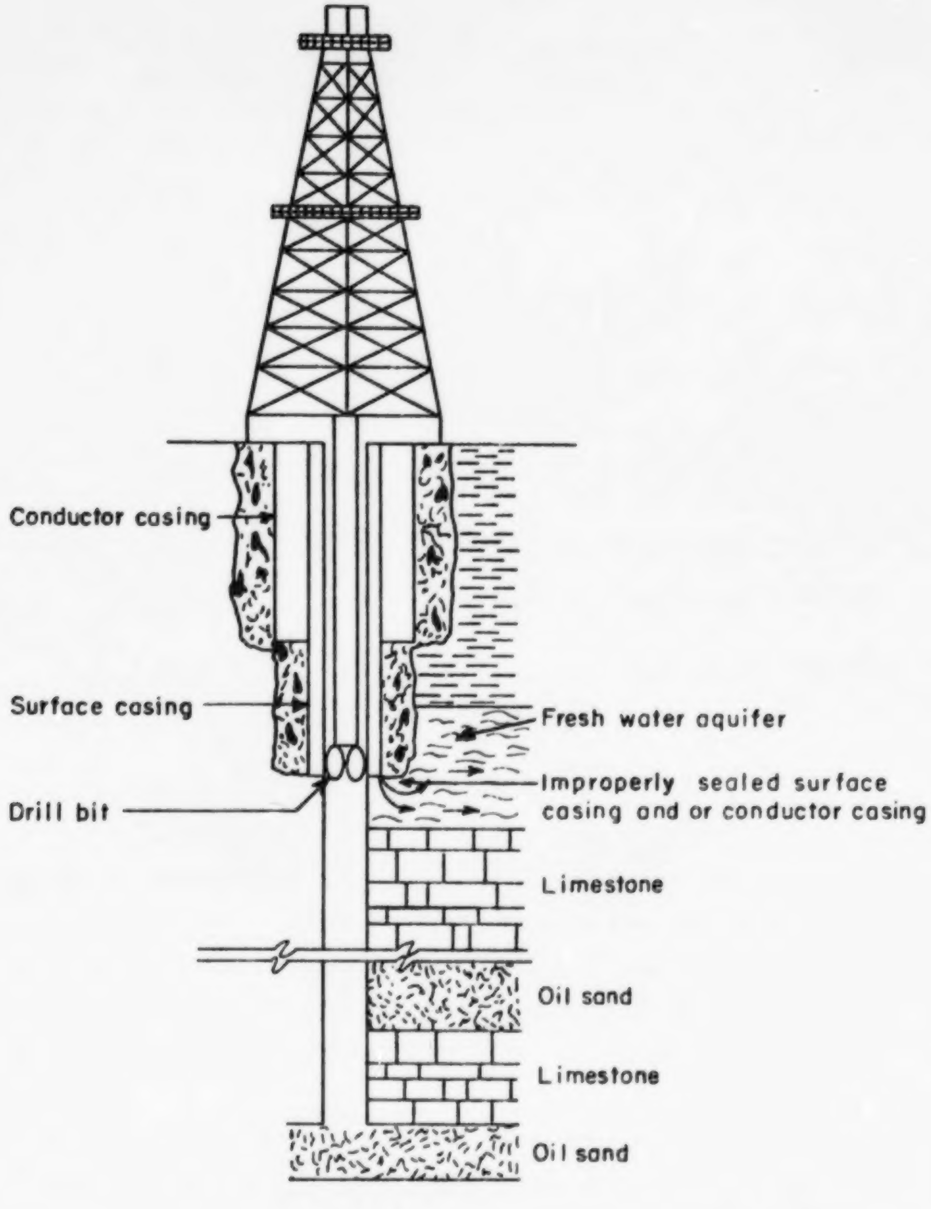
Conductor casing
Surface casing
Fresh water aquifer
Drill bit
Improperly sealed surface casing and or conductor casing
Limestone
Oil sand
Limestone
Oil sand

Figure 2. Illustration of how improperly sealed surface casing and/or conductor casing may provide an entry for a contaminant into a fresh water aquifer.

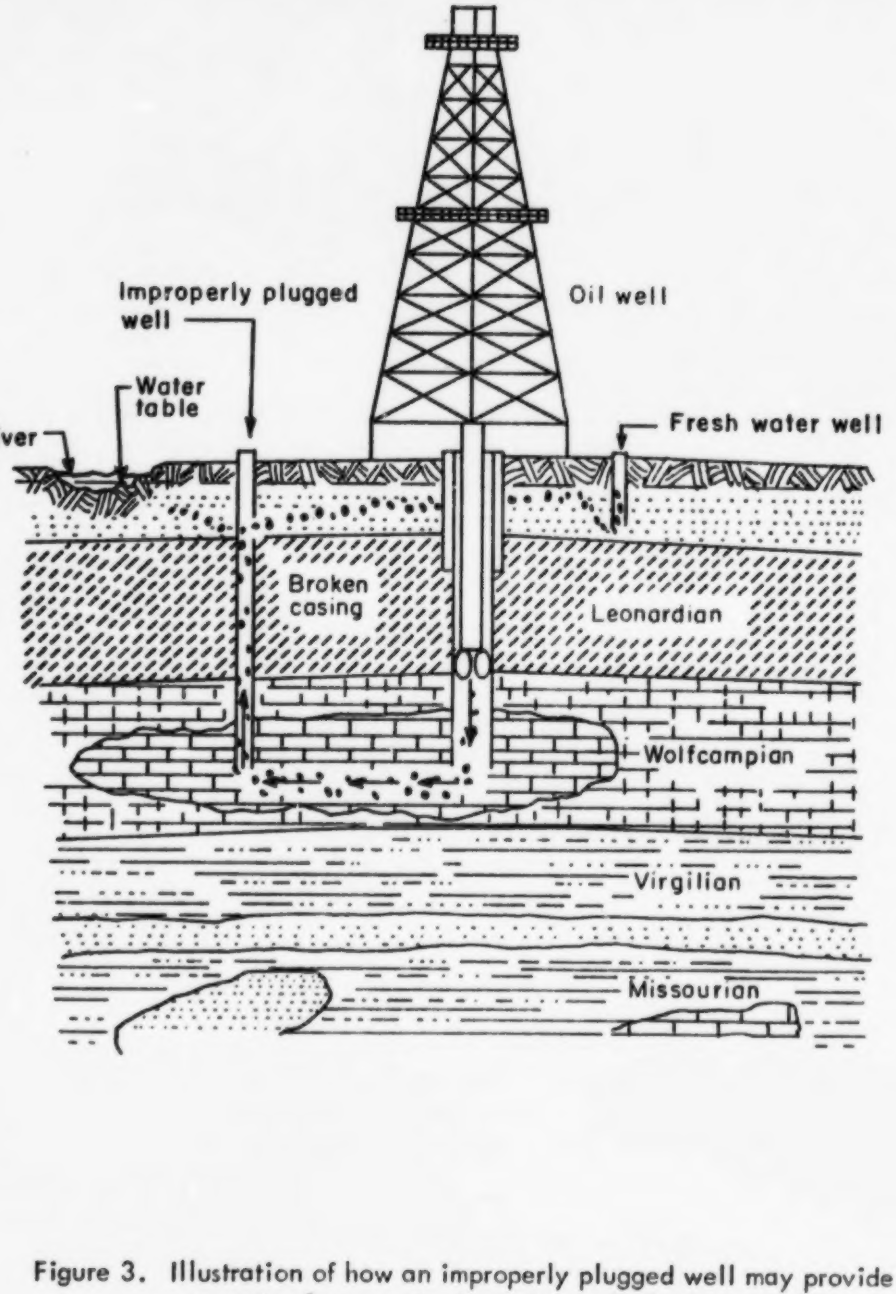
Improperly plugged well
Oil well
Water table
River
Fresh water well
Broken casing
Leonardian
Wolfcampian
Virgilian
Missourian

Figure 3. Illustration of how an improperly plugged well may provide an entry for a contaminant into a fresh water aquifer and eventually into a surface river.

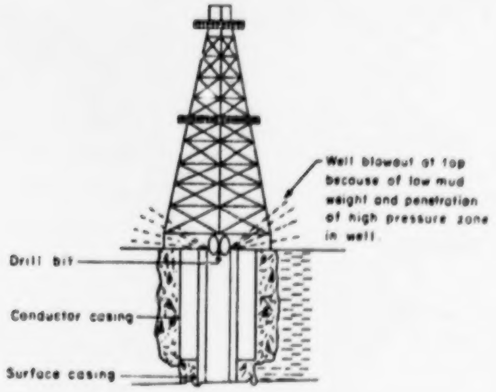
Well blowout at top because of low mud weight and penetration of high pressure zone in well.
Drill bit
Conductor casing
Surface casing

Figure 4. Illustration of a well blowout caused by penetration of a geopressured zone while drilling with inadequate mud weight.

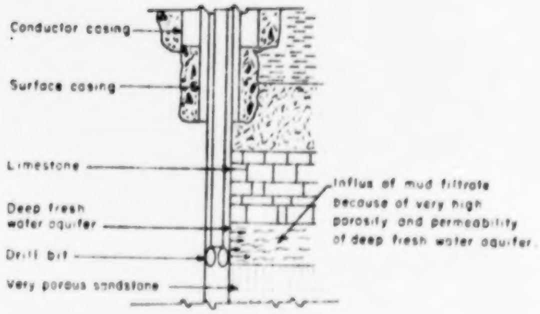
Conductor casing
Surface casing
Limestone
Deep fresh water aquifer
Drill bit
Very porous sandstone
Influx of mud filtrate because of very high porosity and permeability of deep fresh water aquifer.

Figure 5. Illustration of drilling fluid infiltrating into a very porous and permeable fresh water aquifer.

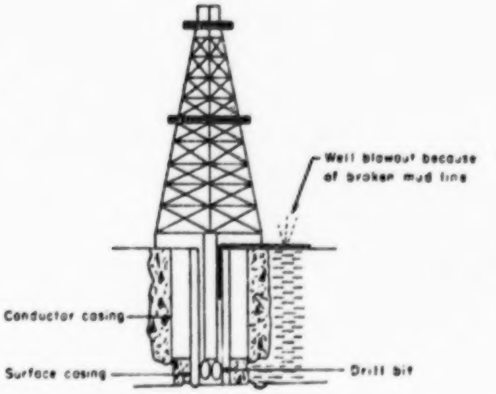
Well blowout because of broken mud line
Conductor casing
Surface casing
Drill bit

Figure 6. Illustration of a well blowout because of a ruptured or broken mud line.

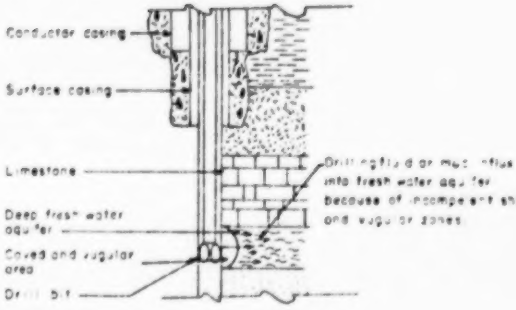
Conductor casing
Surface casing
Limestone
Drilling fluid or mud influx into fresh water aquifer because of incompetent shales and vugular zones
Deep fresh water aquifer
Caved and vugular area
Drill bit

Figure 7. Illustration of drilling fluid contaminating a deep fresh water aquifer because of incompetent shales, cavernous area, or vugular zone.

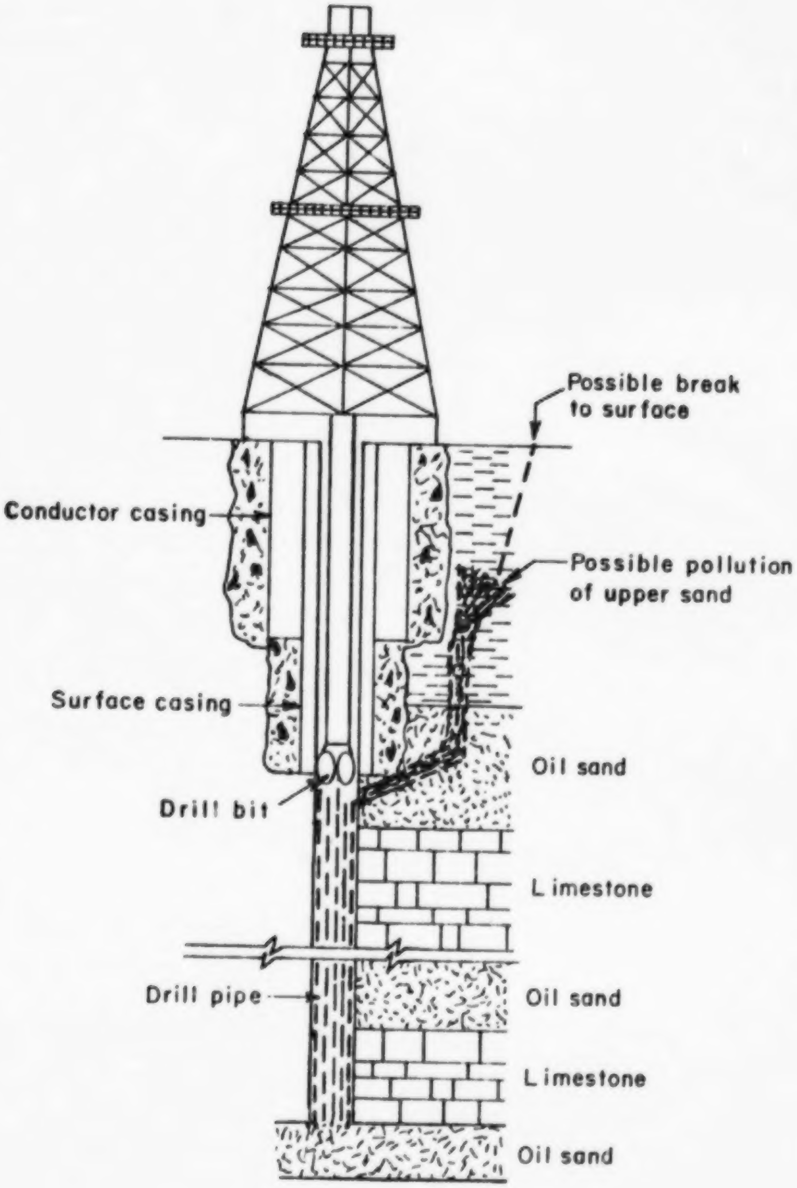
Possible break to surface
Conductor casing
Possible pollution of upper sand
Surface casing
Oil sand
Drill bit
Limestone
Drill pipe
Oil sand
Limestone
Oil sand

Figure 8. Illustration of well blow out into subsurface zone with ultimate contamination of a near surface fresh water aquifer.

Water-Base Drilling Fluids

The type and extent of possible contamination of a ground water is dependent upon the type and amount of drilling fluid that might mix with the fresh water. A water-base drilling-fluid system often is prepared with a natural brine, brackish water, or gypsum-treated water; therefore, it is likely to contain high concentrations of chloride. Any ground water mixing with this type of drilling fluid will be contaminated by the original brine and by the added drilling fluid chemicals. Assuming that the drilling fluid contains 100,000 mg/l of chloride or some other water-soluble contaminant, then 1 barrel of the drilling fluid mixed with 400 barrels of potable ground water containing 10 mg/l of chloride will result in a mixture containing approximately 259 mg/l of chloride, an increase of almost 250 mg/l. The above can be calculated by the following equation:

$$C_M = \frac{V_{DF} \cdot C_{DF} + V_w \cdot C_w}{V_M} \qquad (1)$$

where,

C_M, C_{DF}, C_w = Concentration of water-soluble contaminant in mixture, drilling fluid, and potable ground water, respectively, mg/l;

V_{DF}, V_w, V_M = Volume of drilling fluid, potable ground water and mixture, respectively, bbl.

If the relative volumes of drilling fluid and contaminated water are unknown, the relative volumes can be calculated from the water-soluble contaminant analysis as:

$$(RV)_{DF} = \frac{C_M - C_w}{C_{DF} - C_w} \cdot 100 \qquad (2)$$

$$(RV)_w = 100 - (RV)_{DF} \qquad (3)$$

where,

$(RV)_{DF}$, $(RV)_{W}$ = relative volumes of drilling fluid and potable ground water, respectively, percent.

The water-base systems are those in which water is the continuous phase. Fresh water is used in some systems, and pH of the drilling fluid will range from 7 to about 9.5. This type of system is sometimes used to spud a well.

Brackish water is used in some systems, and the brackish water often is sea water obtained from the open sea or bays. The pH of the system again ranges from 7 to 9.5.

Brine or nearly saturated salt water is used in some systems. The brine can be a natural oilfield brine or it may be a fresh water saturated with salt.

A gypsum-treated drilling fluid is fresh, brackish, or brine water treated with calcium sulfate. A lime-treated drilling fluid has a pH greater than 11; sodium hydroxide or calcium oxide are used.

Oil-Base Drilling Fluids

Mixing of ground water with an oil-base drilling fluid will produce a different type of contamination because oil is the continuous phase and water is the dispersed phase. Oil and water do not mix well, and most oils are almost insoluble in water at low temperatures and pressures. At the present time, diesel oil is most commonly used as the oil phase in oil-base drilling fluids.

Crude oils were used extensively in the past in preparing oil-base drilling fluids. Some heavy crude oils possess a specific gravity of about 1, contain about 5 weight-percent sulfur, and have an overall minimum boiling point of about 270°C. Conversely, some light crude oils contain virtually no elements other than carbon and hydrogen, have 0.8 or less specific gravity, and distill below 270°C. The major nonhydrocarbons in crude oils are basic and nonbasic nitrogen and sulfur compounds and acidic and nonacidic oxygen compounds. Usually the nonhydrocarbons are more highly concentrated in the heavier portions of the crude oils. In an overall classification, most crude oils can be classified as naphthenic, paraffinic, or intermediate; the naphthenic type usually is the heaviest, the paraffinic the lightest.

POSSIBLE POLLUTION FROM NATURAL GAS

Blowouts of natural gas wells can contribute to pollution, especially if the natural gas contains appreciable quantities of hydrogen sulfide. Many gas wells contain enough hydrogen sulfide to pollute fresh water they may contact. Such contact may develop if a well is faulty and communication between the gas zone and an upper fresh-water zone occurs. Brines associated with hydrogen sulfide-bearing gas zones also contain appreciable quantities of the sulfide.

RESIDUAL SALT CONCENTRATIONS BENEATH OR NEAR ABANDONED UNSEALED PITS

Unsealed surface pits that are used to contain drilling fluids used for the disposal of oilfield brines could contaminate fresh surface waters, potable ground waters, and fertile land. Figure 9 illustrates a suction pit, settling pit, and reserve pit which often are used in mixing and storing drilling fluids. Because of chemical and physical phenomena and dispersion, the movement of soluble pollutants from these pits is complex. For example, the soluble pollutants move slowly in relation to the soil water-flow rate, and dispersion effects a displacement which causes the contaminated zone to grow.

The Kansas State Department of Health studied the soils beneath and near an oil unsealed brine disposal pond that had been abandoned for 10 years (ref. 4). During its use, the pond received more than 29,000 metric tons of salts, and most of those soluble salts probably escaped by soil leaching and downdrainage and penetrated below the

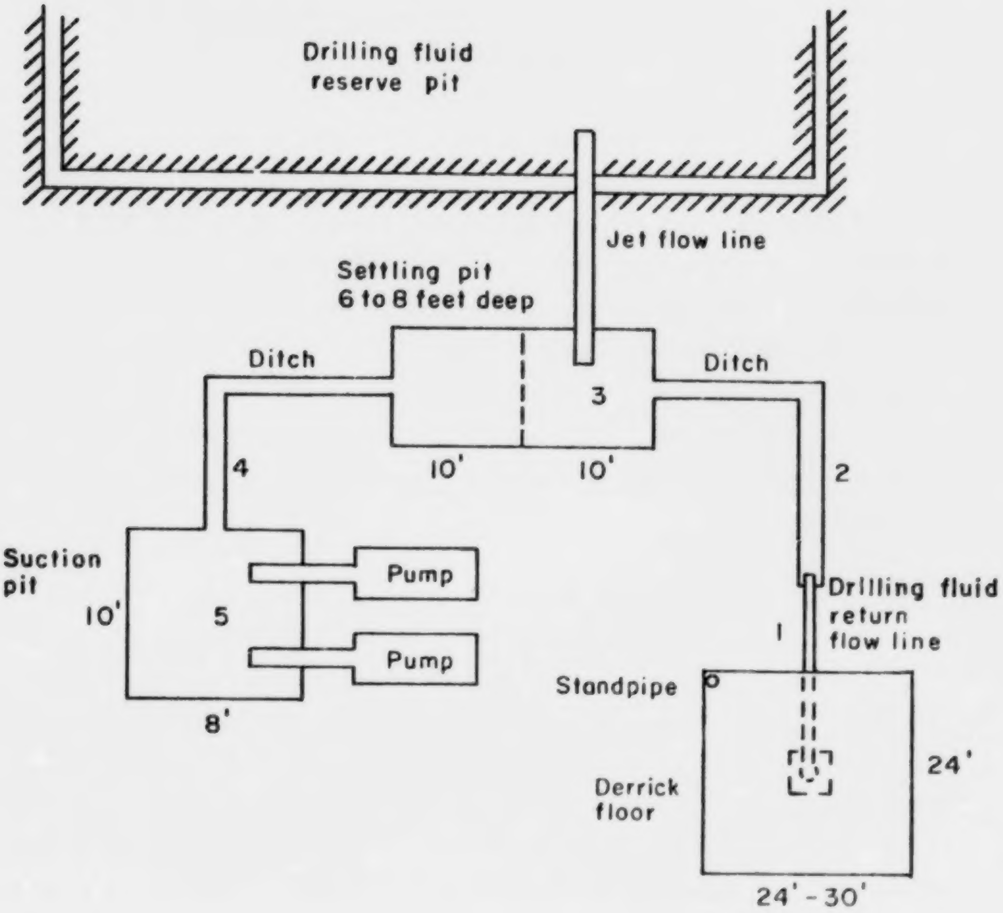
Drilling fluid reserve pit
Jet flow line
Settling pit 6 to 8 feet deep
Ditch
Ditch
3
10'
10'
4
2
Suction pit
10'
5
Pump
Pump
8'
Drilling fluid return flow line
1
Standpipe
Derrick floor
24'
24'-30'

Figure 9. Illustration of suction pit, settling, pit, and reserve pit used in mixing and storing drilling fluid.

underlying limestone formation. Eleven test holes were drilled into the soil and shale beneath and adjacent to the pond, both above and below the natural drainage slope. Chemical analysis of the test-hole core samples indicated that more than 430 tons (about 1.4 percent of the original) of soluble residual salt still remained to be leached out of the soil and shale in the pond area. This amount of soluble or leachable salt remaining in the area indicates that the return of the subsurface water and soil to their prepollution level is a very slow process and may take several decades. Network pollution zones appear to form where formation fracture conjugates occur. Leaching appears to be entirely dependent upon the flushing mechanism provided by meteoric water.

The cation concentrations in the clay minerals were evaluated by X-ray diffraction techniques to trace cation transportation rates. Chloride analysis was selected as the most useful single means of detecting the presence of oilfield brine pollution, but the associated cation concentration should also be determined to formulate a more complete picture. Cation absorption studies are apparently useful in differentiating brine-polluted soil and shale, clay mineral studies provide the information on the environmental characteristics of the pollution media, and cation exchange information aids in explaining the apparent differential transportation rates of ions in brine seepage solutions (ref. 4).

REHABILITATION OF A DRILLING FLUID CONTAMINATED AQUIFER

Consider some of the methods that might be used to rehabilitate a fresh ground-water aquifer that has been contaminated by drilling fluid. A determination must be made to ascertain the type of drilling fluid contaminant, how much of the aquifer is contaminated, and the direction in which the aquifer water is moving and at what rate. With this knowledge, a rehabilitation plan can be organized (ref. 8).

Some possible methods include: containment, accelerated discharge, use, and deep-well disposal. The water in most subsurface aquifers moves slowly. The actual rate is dependent upon many variables. However, assuming that the rate is about 200 feet per year and further and that the movement of a particular aquifer is toward a river, which is about 10 miles from the point of contamination, it then can be calculated that it will require about 260 years for the aquifer to flush the contaminants into the river.

A costly method would be to contain the contaminant by constructing an impermeable underground wall around it. The exact cost of this method is dependent upon the type of wall, depth of aquifer, size of contaminated area, and yearly maintenance costs.

A second alternative is to drill a well into the contaminated zone and pump out the aquifer until the contaminant is removed. The contaminated water must then be disposed of in some acceptable manner, or used.

If the contamination is not too severe, the water might be used for irrigation with or without mixing with fresh water, or the contaminated water might be pumped into a deep well for disposal (refs. 4,8).

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DISCUSSION

DR. RICHARD S. SCALAN (University of Texas, Austin, Texas): I would take exception with Mr. Collin's statement that paraffins are probably the most soluble components in crude oil. Indeed, I would think that the lighter molecular components, aromatics, might be more soluble in water than paraffins.

What is more, if one were going to use crude oil for an oil-base mud rather than something like diesel oil, one would probably have things such as nitrogen, oxygen, and sulfur compounds that would be more soluble than the paraffins.

MR. COLLINS: That is right. Did I say that they were the most soluble?

Yes, the aromatics, such as the benzenes, are more soluble.

MR. T. J. ROBICHAUX (Petrolite Corporation, St. Louis, Missouri): Dr. Giam, I would like to go back to the question that you proposed after the first speaker, concerning the formation of dioxin from pentachlorophenol.

While certainly that is a possibility under the conditions, there are certain mitigating factors that have to be considered. One is the concentrations that you are dealing with in using penta as a bactericide in a drilling mud; you are dealing with concentrations in the neighborhood of a hundred parts per million.

The other thing that you have to consider is the residence time at a high temperature as the mud is circulated around; while it may penetrate a high temperature zone, it does not stay there very long.

And third, if by some natural forces you did cause or did form a concentration of dioxin of concern, there are so many opportunities for that to be modified while in the mud itself--either absorb to a surface, or in some way be impeded from returning to the environment where it could become a possible entrant in a problem.

MR. ROBERT B. ALLRED (Sun Oil Company, Richardson, Texas): Mr. Collins, I won't question where you got your prices of drilling fluids. But if you could run one for $200 a day, I believe I can put you to work at 11:00 o'clock.

MR. COLLINS: I am going up, slightly. Costs depend on the size of the rig and on other factors. The cost I quoted is only an average figure, and may not account for recent inflation.

CHAIRMAN GIAM: Can I come along too?

MR. JAY B. SIMPSON (Baroid Division, N L Industries, Inc., Houston, Texas): I would like to comment on the crude oil. A crude oil would be very rarely used in preparation of an oil mud these days. On the use of the produced saltwater--by far most of the water-based muds are made from freshwater. Although many are made from produced water, percentagewise, the vast majority of the water-based muds would be mixed with freshwater.

MR. COLLINS: Well, I took the statement from the literature, so I have no firsthand knowledge.

MR. HARRY L. HARRISON (A. C. Drilling Specialties, Odessa, Texas): I would like to ask Mr. Collins if there have been any studies in a polluted system, in a polluted freshwater or fresh ground-water system where the sweep is considered, the amount of the dilution due to sweep away from the area, and the volumes that would have to be considered.

MR. COLLINS: We have not made any studies of this type.

MR. HARRISON: I think we should look at these things carefully because it is very easy to say you polluted that stream when you poured a barrel of brine water into it or a freshwater sand. But as these materials move out away from the source, they are considerably diluted and we run into a cost thing here. I think it should be considered.

MR. COLLINS: Yes, they would be diluted.

MR. JAMES W. WINFREY (petroleum consultant, Houston, Texas): In the interest of accuracy, Mr. Collins, I would suggest that in talking about the number of rigs running, we would sure like to see 3,000 rigs running in the United States. But there are only about half that many now. As you mentioned, with the changes in the depletion allowance, it will probably drop off. The average now is somewhere in the order of a little over 1,500. Then in one of your slides you really touched a nerve where you showed surface casing set above a freshwater zone. That has been against regulations in the States of Texas and Oklahoma, in all of the big oil-producing States, for many, many years. And you have to get approval, of course, for a casing setting depth to be sure that you are below a freshwater zone.

So while you can have underground blowouts (and there have been underground blowouts due to incompetent cement where it channelled back up around the surface casing) you just do not set your surface casing above a freshwater zone.

MR. COLLINS: I realize there are these laws. However, in some cases deep, freshwater aquifers exist. The slide was just an example of a possibility.

MR. PAUL D. FLEISCHAUER (The Aerospace Corporation, Los Angeles, California): I would like to ask about the question that has been in the news. Lately there has been a lot of controversy about carcinogens in some of the water supplies in Los Angeles and other cities. Do you have any data on chlorination reactions that occur in the water table, say, on the surfaces of particulates or any homogeneous reactions?

MR. SHEW: You mean to form those chlorinated compounds?

MR. FLEISCHAUER: Right.

MR. SHEW: I am not sure what they are proposing. I believe they are claiming that these arise from, or are a result of, chlorination of the naturally occurring organics in ground water, for example, or organics that get into freshwater supplies before it is chlorinated.

Now, I am just not sure if it will hold or not. I am not sure that this has been shown absolutely to be the source of chlorinated hydrocarbons or not. I am anxious to wait 6 months and find out if this holds up.

GENERAL CHAIRMAN FISHER: The chlorinated materials which are being picked up in water supplies are, in fact, from what is properly called an unknown source. It is not really thought that very many of these, at least, are natural in origin. Some of them are clearly environmental contaminants in their own right, largely from pesticidal uses, and possibly from some of the other types of disinfectants which were discussed here yesterday. Although, as we also pointed out, the well applications of these disinfectants are really very minor compared to their many other applications.

However, many of the materials--and especially those which are being found in larger quantities, like chloroform and so on--are almost certainly artifacts from water purification procedures, either in industrial wastewater treatment or in the actual water purification plants themselves, where various organic compounds, either anthropogenic or natural, are in the incoming water. When you chlorinate the water, these materials do react with the chlorine in various ways, and some of the reactions are very simple ones; anybody who took elementary organic chemistry can explain how chloroform can arise from a large number of compounds that you could find all over the place.

And I think it will hold up pretty well; in fact, most of these materials are arising from our water purification practices, in combination with our rather gross pollution of the waters before they get to water purification plants.

MOBILITY OF WELL-DRILLING ADDITIVES IN THE GROUND-WATER SYSTEM

Michael D. Campbell and George R. Gray, Ph.D.*

Abstract

Components of the drilling fluid may enter an aquifer through any of the avenues available to surface water, such as the outcrop, stream runoff, percolation, and abandoned wells. From the well bore, materials may enter ground water as a consequence of lost circulation, seepage, filtration, or blowout. The contaminating material may be gas, liquid, or solid, and in the form of coarse to fine solids, colloidal suspensions, or solutions. The subsequent behavior and characteristics of the entering substance are determined not only by its initial properties but also, to a large extent, by the properties of the reservoir rock and the interstitial water. Physical separation of suspended solids depends on particle size, shape, concentration, and density and on the pore geometry of the aquifer. The chemical composition and the microorganisms present in the ground water may cause precipitation and decomposition reactions. Adsorption on surfaces and other interfacial phenomena in the reservoir are particularly important and are of a complexity seldom, if ever, met in the laboratory. Movement of drilling fluid materials into the aquifer will be governed by the geohydrologic conditions present. Flow conditions are controlled by the aquifer permeability and the pressure gradient. Such flow may be modified by the introduced substances and their effect on existing conditions in the aquifer.

INTRODUCTION

The purpose of this paper is to examine the factors involved in the movement of drilling-fluid components in the ground-water reservoir. Components of the drilling fluids will be considered generally and no attempt

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will be made to deal with specific substances. Examples of the important mechanisms involved in the movement of liquids, solids, and gases from the borehole into the formation will be discussed.

Some definitions may aid in delineating the scope of this review. An "aquifer" is a geologic "formation, group of formations, or part of a formation that contains sufficient saturated permeable material to yield significant quantities of water to wells and springs" (ref. 36). A "drilling fluid" is a material used as an aid to tools in the excavation of earth. Accordingly, the drilling fluid may be employed with such varied tools as augers for foundation borings, and cable tool and rotary drills for ground water and petroleum exploration and for mineral exploration and mine development. Composition of the drilling fluid may range from dry air or potable water to diesel oil containing gellants, emulsifiers, and several types of suspended solids. A "contaminant" is any introduced substance, or product of an introduced substance, that modifies the properties of the initial ground water to such an extent that its usefulness in the desired application is impaired.

This discussion is concerned with the movement of any substance that enters the ground-water reservoir as a consequence of the drilling operation, whether such a substance is a drilling-fluid additive, or fluids or earth materials derived from the excavation.

The term "drilling fluid" embraces an extremely variable composition of matter. Characterized according to the principal component as "gas," "water," or "oil," usually two (somethimes all three) fluids are present, along with suspended and dissolved materials. If the major component is a liquid, the drilling fluid is called "mud" and is broadly classed as "water mud" or "oil mud." Prior publications (refs. 2, 22, and 23) and other papers presented at this conference deal with the components of drilling fluids in some detail and they need not be reviewed here.

CONTAMINATION FROM THE SURFACE

Contamination of ground water from the surface may originate in earthen pits in which mud is placed, either for circulation or storage; from leaching of cuttings; from spilled mud or ingredients; from containers for the additives, and from mud and materials discarded on completion of drilling operations.

In drilling deep wells, practically without exception the mud is contained in steel tanks. The cost of the mud, as well as possible reuse or sale of excess mud, justifies adequate facilities for storage. Many small rigs also use steel tanks for the mud being circulated, although surplus mud is stored in earthen pits or discarded on the surface (figure 1). When earthen pits are used in the active mud system, if the surface exposed in the dug pit is not clay, the surface is sealed with bentonite or other clay before mud mixing is begun (figure 2).

Bulk handling of the principal mud constituents has greatly reduced spillage and waste of materials. More attention should be given, however, to the handling of water-soluble additives. Not infrequently the contents of opened bags containing caustic soda, lignosulfonates, or the like, will become caked and will be discarded, thus becoming a potential source of ground-water contamination under certain geologic conditions. "Good housekeeping," therefore, is a highly desirable practice.

The cuttings separated at the surface and the adhering drilling fluid are regarded as waste products. A considerable quantity of earth is excavated during the drilling operation. For example, in drilling a municipal water well in Houston, Texas, to a depth of 2,500 ft., over 14,000 cubic feet of earth weighing over 1-1/2 million pounds must be brought to the surface. Usually cuttings are not regarded as a source of ground-water contamination, with the exception of soluble salts, such as halite or gypsum. Disposal of cuttings and mud in some locations is an expensive item in well drilling. In the Los Angeles basin, for example, cuttings and excess mud must be hauled to designated sumps for disposal. In The Netherlands, the drill site is covered with a concrete apron surrounded by dikes. All waste water, in addition to cuttings and mud, must be removed from the location.

Components of the drilling fluid may enter ground water through any of the routes available to surface water, such as the outcrop of the aquifer, streams, percolation, and abandoned wells. Shallow aquifers are often exposed to contamination through construction borings; excavations for foundations, sumps and mud pits, and by drilling relatively shallow holes for seismic and mineral exploration.

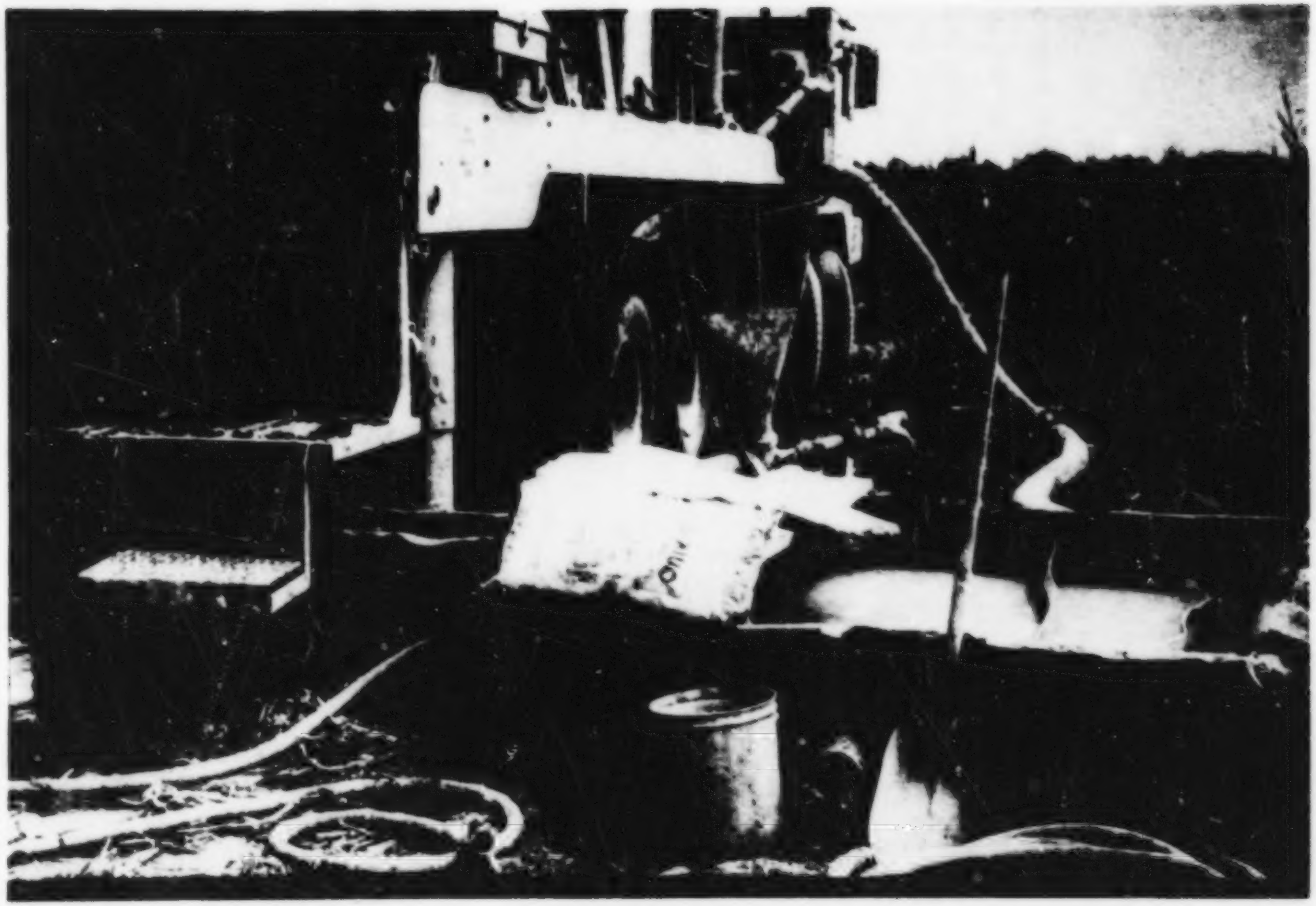


Figure 1. Mud tanks for water-well drilling.

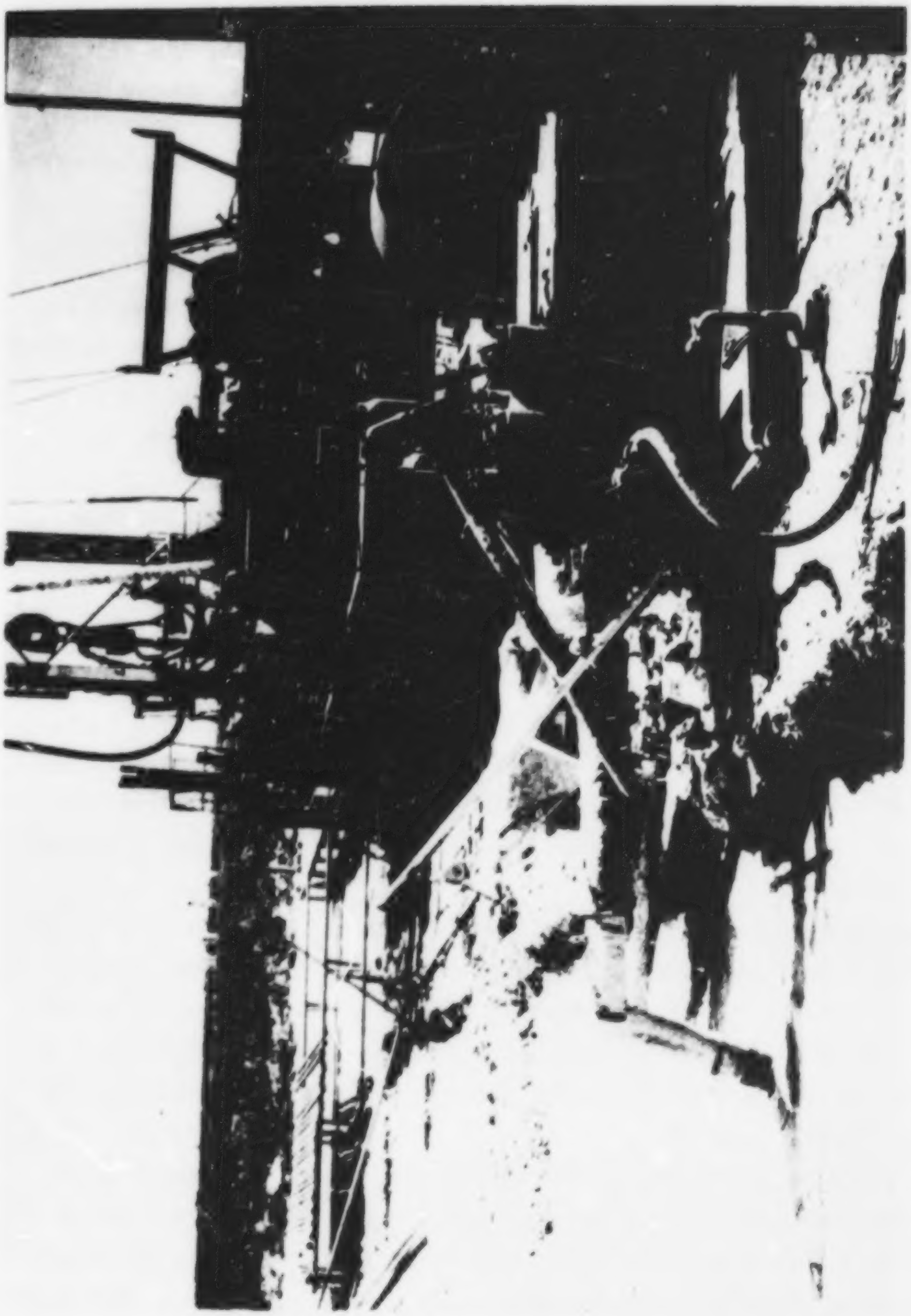


Figure 2. Bentonite-scaled mud pit for oil-well drilling.

In the construction of earthen mud pits, attention is given to avoiding the loss of whole mud. After mud has been prepared in an earthen pit, seepage of liquid and percolation into an aquifer is controlled by the filtration characteristics of the mud. Chemicals spilled on the ground, however, do not have this limitation on their mobility.

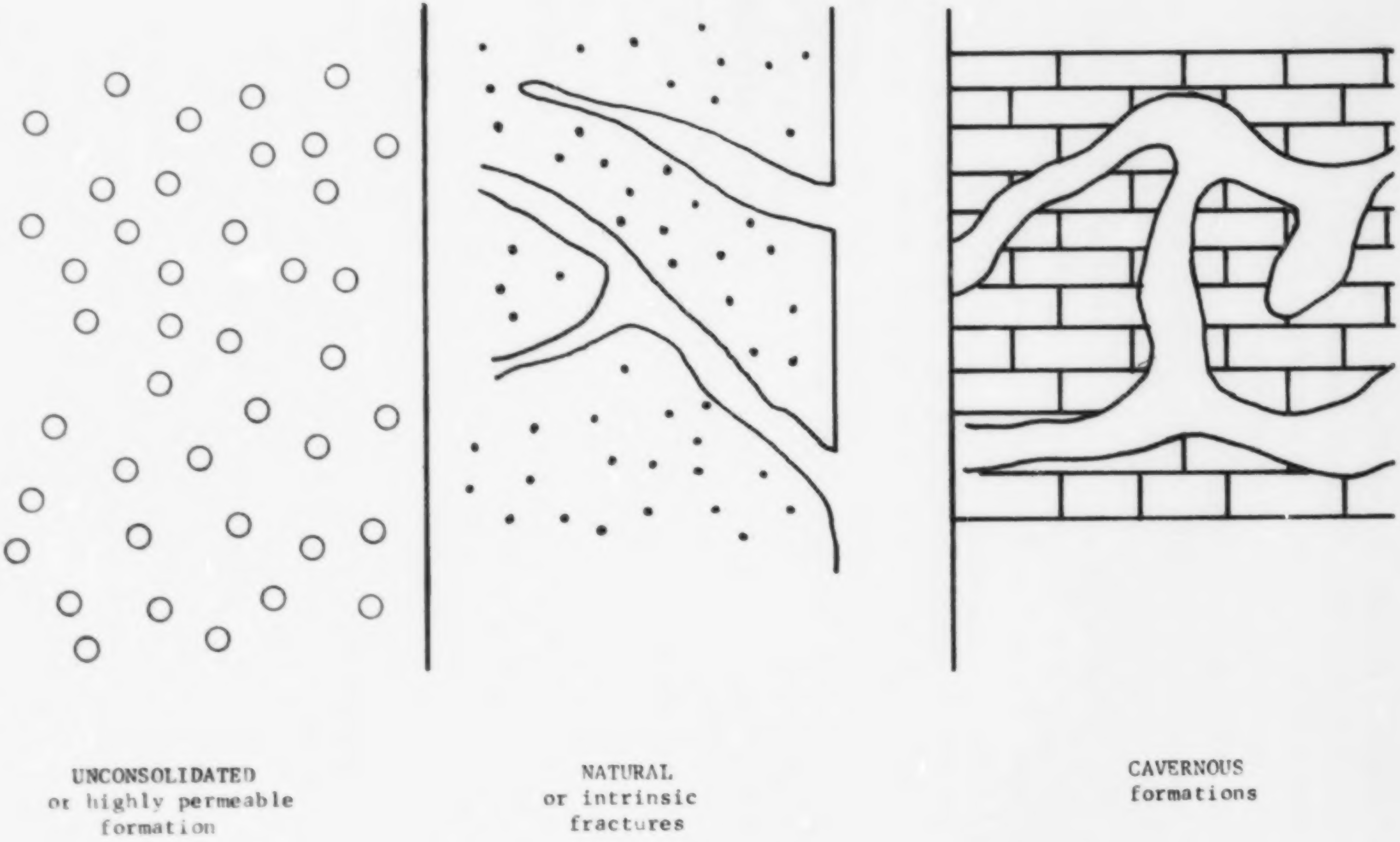
CONTAMINATION FROM THE BOREHOLE

The most obvious mechanism for the contamination of an aquifer by drilling fluid occurs when circulation is lost. Lost circulation has been the subject of numerous studies (refs. 9, 29, and 38). Almost every material that could be poured, pumped, or pushed into the borehole has been proposed as a remedy (ref. 30). Nevertheless, loss of circulation continues to be one of the most serious and widespread problems in drilling.

For loss of circulation to occur there must be openings in the formation large enough to accept the whole mud, and sufficient pressure must be exerted to force the mud into the openings. "Lost circulation" is thus distinguished from "loss of water," which takes place when a permeable zone is encountered while drilling with water, and from "water loss," or filtration of liquid through a filter cake of mud solids formed on a permeable formation. Formations that can take whole mud can be classed broadly as: (a) cavernous, such as limestone containing solution channels; (b) loosely consolidated, such as coarse sands and gravels, and (c) fractured, jointed, and fissured formations (figure 3).

To stop loss of mud, the openings must be plugged with a material containing particles of such sizes, or having such consistency, that greater resistance is offered to entry of the mud than is presented by flow up the annulus of the borehole. Sometimes this condition cannot be realized. Drilling may be resumed and the cuttings carried into the zone of loss by the drilling fluid.

However, under some conditions, contaminants may enter avenues of communication with other wells, streams, etc. These condtions are where open channels would allow "lost circulation" materials and drilling fluids direct communication with distant points. The possibility exists that groundwater contamination could occur under some conditions. One case of migration


UNCONSOLIDATED
or highly permeable
formation
NATURAL
or intrinsic
fractures
CAVERNOUS
formations

(After Messenger - 1968)

Figure 3. Types of formations that can take whole mud.

of what is in fact a component of a drilling-fluid additive was reported by Sweet and Fetrow (ref. 43). A case of ground-water pollution was reported involving wood-waste disposal (i.e., lignin-tannin, which is a common drilling-fluid additive in oil-well drilling operations).

While drilling with water, seepage may occur into porous, permeable formations exposed in the borehole. Finely-divided cuttings carried by the water enter the openings and, as individual pores become bridged by the larger particles, successively smaller particles are filtered out. Clay or other material of colloidal dimensions converts seepage into filtration. The passage of liquid into the formation then becomes dependent on the amount and physical state of the colloidal material in the drilling fluid and not on the permeability of the formation (ref. 10). In porous media, the thickness and character of the filter cake precondition the extent of liquid invasion into the formation during the drilling operation. When circulation is stopped, cake thickness continues to increase but at a decreasing rate (figure 4). Studies of the filtration of oil-field muds have shown the permeability of the filter cakes to be in the range of 10^{-3} to 10^{-5} millidarcys (refs. 5, 11, and 46). Estimations have been made of the rate of invasion of filtrate into sands in the course of drilling (refs. 21 and 47). A radius of invasion of nearly 2 feet was calculated for a period of 138 hours between penetration of a sand and cementing of casing. More than 90 percent of the total filtrate flowed from the mud while it was circulating during about 75 percent of the elapsed time (ref. 21.)

The most spectacular method of introducing contaminants into ground water is by means of a blowout. This uncontrolled entry of fluids into the borehole may force gas into shallow aquifers and cause water wells to begin flowing or even to blow out. Keech (ref. 32) cites a dramatic case history of widespread ground-water contamination by a subsurface natural-gas well blowout in the vicinity of a number of water wells. In another example, the effects of a blowout in the Bammel field north of Houston, Texas, are still evident after 30 years. Water wells drilled several miles from the site of the blowout often require prolonged completion operations because gas coming out of solution in the water interferes with the functioning of the pumps.

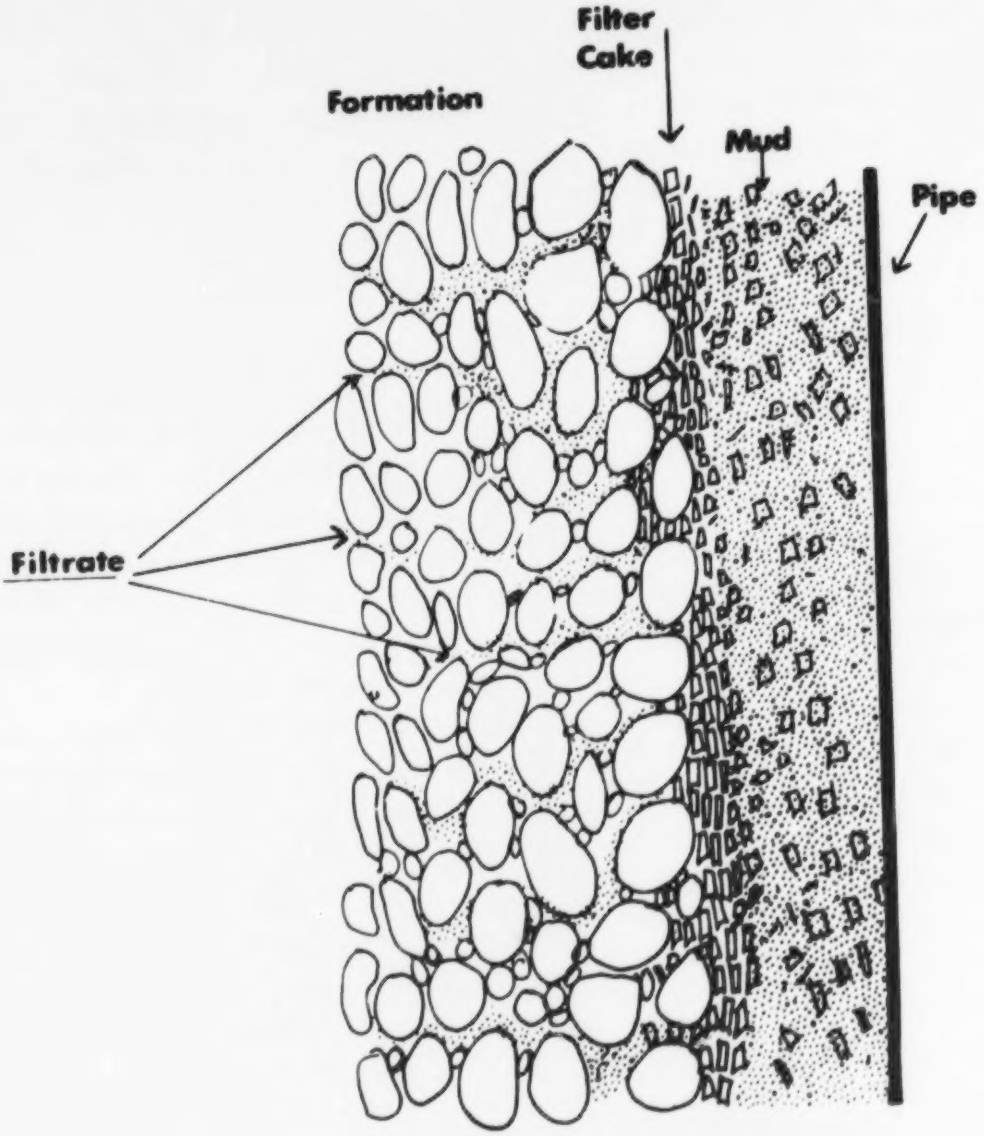

Filter Cake
Formation
Mud
Pipe
Filtrate

Figure 4. Cross section showing borehole and adjacent formation (note mud-filtrate invasion characteristics).

Contaminants can enter the ground-water reservoir as wells are drilled, during their operational life, or following their abandonment. Possibly of greatest potential consequence is the nearly unavoidable introduction of biological agents into the aquifer via drilling fluids. Subsequently, the growth of certain types of bacteria that cause corrosion and incrustation may be an important factor in contamination of aquifers. The routes by which contaminated water can enter the ground-water reservoir through faulty oil or water well construction have been briefly explored by Collins (ref. 15) and by Campbell and Lehr (ref. 13) and need not be treated here.

IMMOBILIZATION OF SUSPENDED SOLIDS IN THE AQUIFER

As has been shown, contaminating substances from drilling operations may enter ground water from the surface or from the well bore. The material may be gas, liquid, or solid. It may be in the form of coarse to fine solids, colloidal suspensions, or solutions. It may be stable or unstable; reactive or unreactive. The subsequent behavior of the entering substance is determined not only by its properties but also, to a large extent, by the properties of the reservoir rock and the interstitial water.

Except under very unusual conditions, particles that will be retained on 200-mesh sieve--the API designation for sand (ref. 1)--can be expected to be removed near the point of entry into the aquifer. Particles having an effective diameter less than 74 microns (200-mesh) also will be subject to gravitational effects that will decrease in importance as the particles become smaller. Sedimentation is not a significant factor in the separation of particles smaller than one micron (figure 5).

The importance of filtration in industrial processes has led to numerous studies of the mechanism. Herzig, Leclerc, and LeGaff (ref. 26) cite 74 references in their examination of the flow of suspensions through porous media. The authors point out that several mechanisums are involved, namely: (a) the contacting of particles with retention sites, (b) the fixing of particles on sites, and (c) the escape of previously retained particles. Factors involved in the system are: (a) the flow rate, viscosity, and density of the carrier fluid; (b) the concentration, size, and shape of the suspended particles, and (c) the geometry of the porous medium.

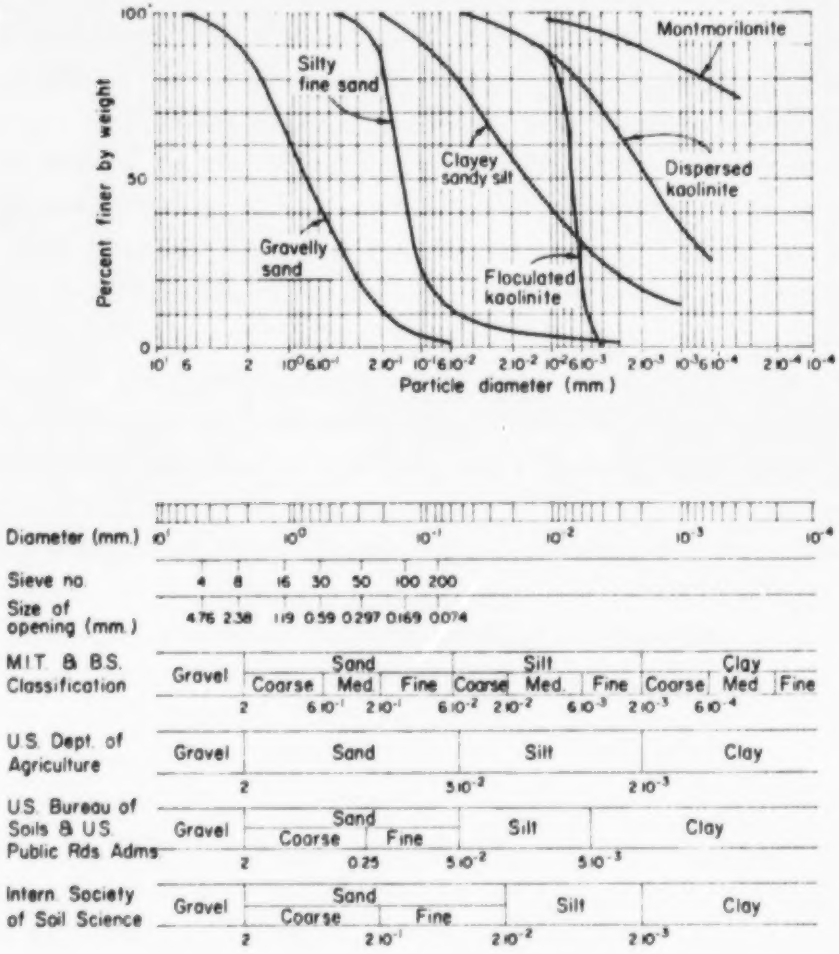


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Figure 5. Typical grain-size distribution curves for various soils with major used classification. (Bear - 1972).

Retention sites can be classed as: (a) surface of a grain making up the bed, (b) crevice between the surface of two grains, (c) constriction and, (d) cavern, or sheltered area formed by several grains (see figure 6a). Forces that hold the particle immobilized include: (a) axial pressure of the liquid, as at a constriction; (b) friction forces, as on a particle wedged in a crevice; (c) surface forces: Van der Waals forces of attraction, and electrostatic or electrokinetic forces which are either attractive or repulsive dependent on the system, and (d) chemical forces, which may involve chemical bonding between the particle and the surface. The process of capture may involve: (a) sedimentation; (b) inertia, i.e., the particles cannot follow the changing path of the liquid; (c) hydrodynamic effects caused by nonuniform shear field and nonsphericity of particles; (d) direct collision with convergent pore walls; and (e) diffusion by Brownian motion into areas not flushed by the suspension (see figure 6b).

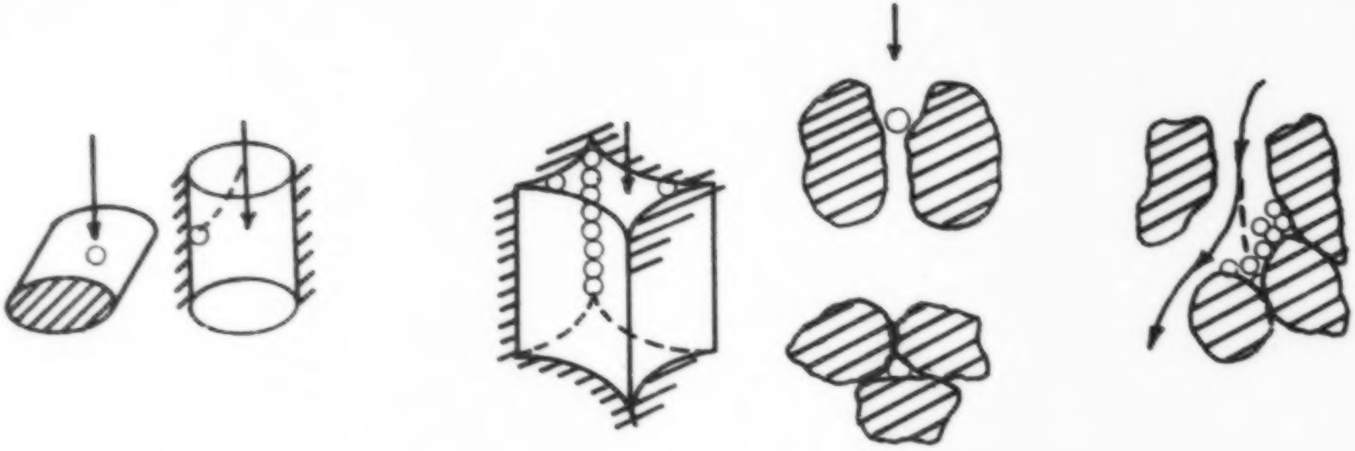
"The flow of suspension through porous media is a very complex phenomenon owing to the diversity of the mechanisms involved" (ref. 26).

MOVEMENT WITHIN THE AQUIFER

Drilling-fluid filtrate invasion in highly permeable sands often appears from electrical logs to be less near the base of the sand than near the top. Doll (ref. 18) concludes that filtrates rise in the sand after passing the filter cake barrier at the hole wall. This, of course, assumes that the filtrate density is less than the denisty of the ground water and suggests that if the density of the ground water is higher than the density of introduced material, the invasion would be strictly gravity controlled. The filtrate would then invade the lower part of the aquifer more rapidly than at the top.

In a study on deep-well waste disposal and waste surveillance, Kazmann (ref. 31) has demonstrated that the density difference between the ground water and the introduced carrier fluid clearly dictates the character of the invasion front with time.

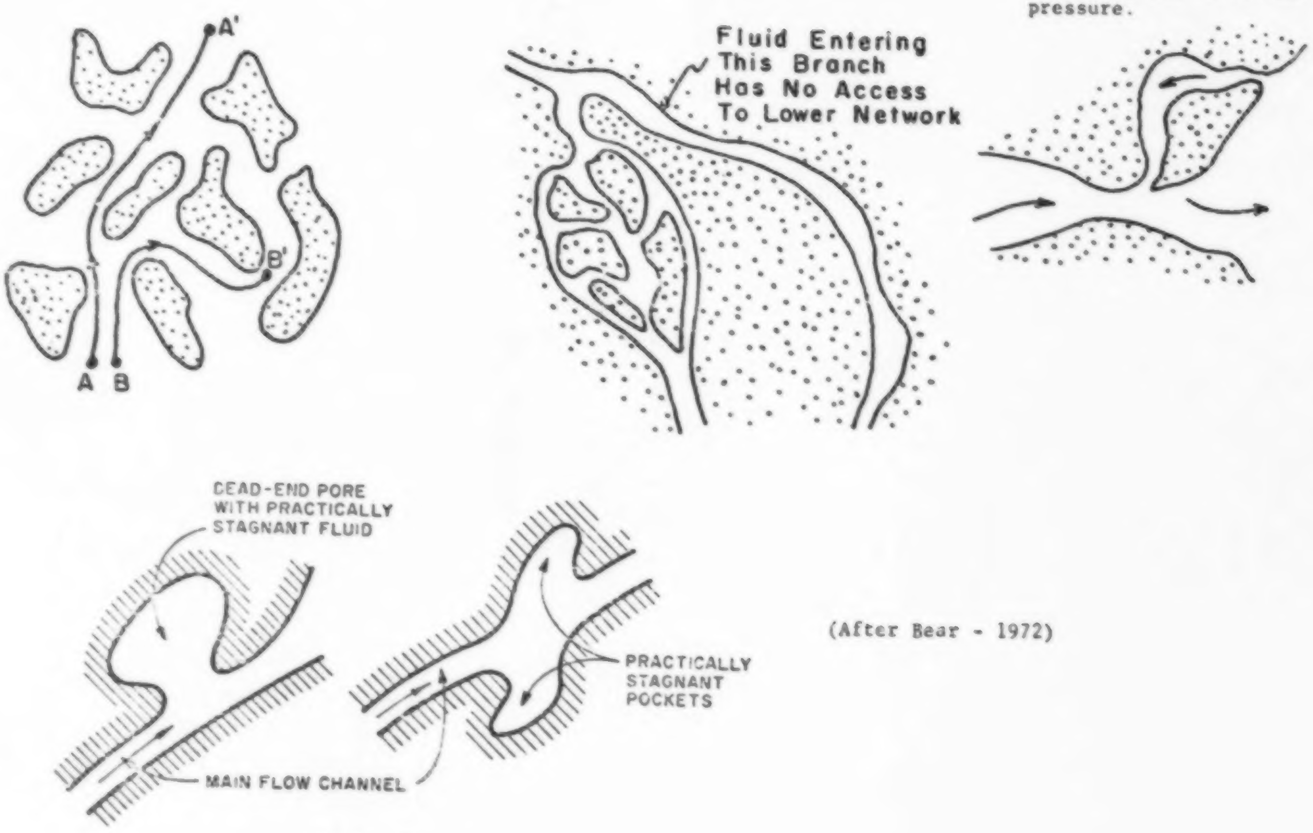
Once fluids and solids pass the filter cake and hole wall into the formation, invasion characteristics of the carrier fluid are affected by many physical, chemical, and biological factors. Numerous macro- and microformational factors affect its path, its rate of flow, and its chemical composition. Information on the course of contaminants in the ground-water system is now voluminous and hence will not be reviewed in detail at this



SURFACE SITES CREVICE SITES CONSTRICTION SITES CAVERN SITES

(After Bear - 1972)

Figure 6a. Classification of retention sites.



Mixing caused by obstructions

Incomplete connectivity of medium

Recirculation caused by local regions of reduced pressure.

Dead-end pores

(After Bear - 1972)

A'
B'
A
B
Fluid Entering This Branch Has No Access To Lower Network
DEAD-END PORE WITH PRACTICALLY STAGNANT FLUID
MAIN FLOW CHANNEL
PRACTICALLY STAGNANT POCKETS

Figure 6b. Typical groundwater flow paths in porous media (micro-range) and cavernous media (micro- to macro-range).

time (ref. 12). However, some of the features pertaining to the potential behavior of drilling fluids within the ground-water system will be explored.

Although open-channel, ground-water flow, e.g., in joints, interconnecting solution channels, fault traces, etc., is not uncommon in the subsurface, porous media flow is emphasized here because of its wide applicability to the major aquifer type--sands, sandstone, etc. The physical aspects of ground-water flow are of fundamental importance to a discussion of mobility of contaminants.

Bond (ref. 6) discusses flow patterns of variable-density ground water and the effects of troughs formed by permeability barriers within aquifers and the effects of structural troughs, saddles, anticlines, and synclines. Childs, et al. (ref. 14) explore the concept of a "waste plume" and suggest that the plume pattern may be complex and may not follow regional ground-water flow, as indicated by other workers (ref. 40). See figure 7.

Ground-water flow through porous media is characterized by laminar flow at low Reynolds numbers (Re), where gradient is held constant. Viscous forces predominate and the Darcy Law is valid. As Re increases, a transition zone is encountered at the lower end; the laminar regime with viscous forces predominating passes to another laminar regime characterized by inertial forces. At the upper end of the transition zone, a gradual passage to turbulent flow is observed. Darcy's Law is not valid in the transition and turbulent zones (ref. 4). Average ground-water flow rates vary widely depending on gradient, permeability, and other geologically-controlled factors.

It is clear that the laminar flow is of predominance in the porous media under consideration here and that it simplifies the effects of the flow regime on the chemical and biological parameters within the aquifer.

Flow paths, when encountering changes in permeability (or changes in ground-water density), will be refracted according to the tangent rule, whereas light is refracted according to the sine rule (ref. 16). See figure 8. This, of course, will affect the chemical and biological parameters to be discussed later. Suffice it here to state, however, that an abrupt change in flow direction may affect one or more characteristics of the carrier fluid, including any introduced contaminant.

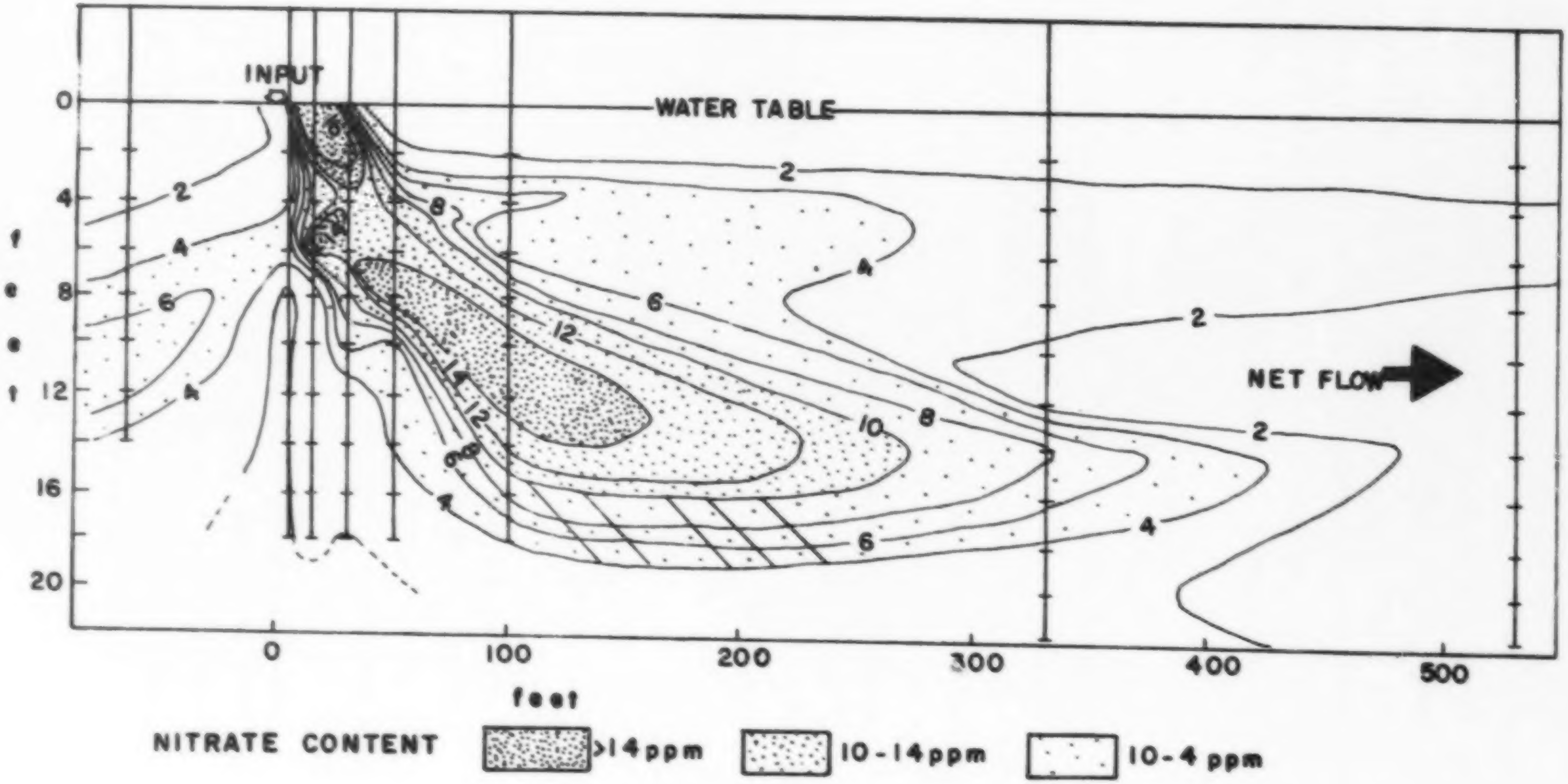
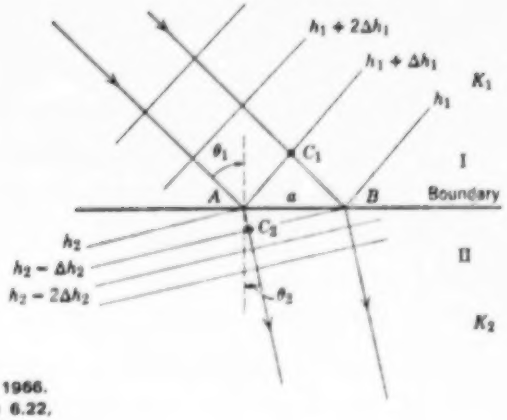


Figure 7. Cross section of a waste plume of nitrates (After Childs, et al., 1974)



$h_1 + 2\Delta h_1$
$h_1 + \Delta h_1$
h_1
K_1
θ_1
C_1
I
A
a
B
Boundary
h_2
$h_2 - \Delta h_2$
$h_2 - 2\Delta h_2$
C_2
θ_2
II
K_2

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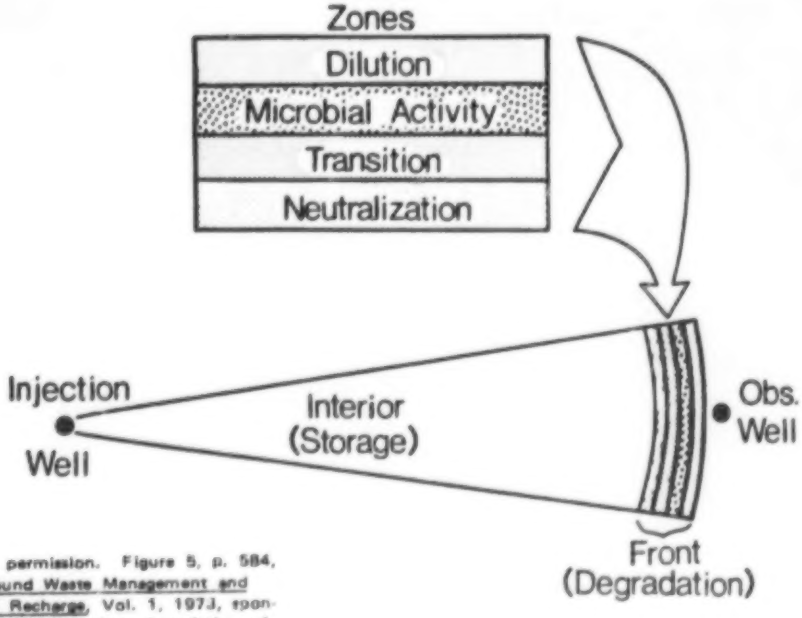
p. 197, Hydrogeology.)

Figure 8. Refraction of streamlines (Davis and DeWiest - 1966).



Zones
Dilution
Microbial Activity
Transition
Neutralization
Injection
Well
Interior
(Storage)
Obs.
Well
Front
(Degradation)

Used by permission. Figure 5, p. 584, Underground Waste Management and Artificial Recharge, Vol. 1, 1973, sponsored by The American Association of Petroleum Geologists, U.S. Geological Survey, and International Association of Hydrological Sciences.

Figure 9. Proposed geochemical model of waste after injection, into subsurface. (Leenheer and Malcolm - 1973).

The concept of dispersion of miscible fluids in porous media has received considerable attention during the past several years, especially with regard to ion exchange in soils, artificial recharge, liquid-waste disposal operations, seawater intrusion into coastal aquifers and seepage from canals and streams into and through aquifers (refs. 7, 8, 27, and 39).

Marino (ref. 37) explores the mathematical framework of simultaneous dispersion and adsorption of a solute within a homogeneous and isotropic porous media in steady, unidirectional flow fields. He concludes that in such conditions the dispersion system is considered to be adsorbing the solute at a rate proportional to its concentration. Mass transfer due to adsorption appears to play an important role in mass transport within natural flow systems.

In general, the mobility of any contaminant introduced into the ground-water system is largely dependent on the capacity of the matrix material within the porous media to adsorb the dissolved substances. However, Sigmor (ref. 42) suggests that movement into the aquifer is subject to limitations caused by degradation of the hydraulic conductivity in the porous medium. As previously mentioned, a reduction in hydraulic conductivity (or permeability) is caused by the retention in the porous media of suspended clay minerals, among other fine minerals, by means of (a) interstitial straining, (b) gravitational settling, and/or (c) adhesion and adsorption.

It is apparent that sensitive flow thresholds exist that may play some role in the chemical reactions and biological activity in an aquifer invaded by foreign materials and carrier fluids and gases. In natural, undisturbed ground-water systems, formation clogging by bacterial growth products occurs when the introduced fluid contains dissolved organic materials and bacterial growth conditions are favorable. Edwards and Monke (ref. 19) studied flow of clay suspensions (similar to some drilling fluids) through a silica porous medium and suggest that bacteria may provide a natural electrical link between the net negatively charged silica and bentonite clay particles.

REACTIONS WITHIN THE AQUIFER

The above discussion of flow through porous media has not considered the interaction between the suspended particles and substances present in solution. The chemical characteristics of ground water are strongly affected by the solids, liquids, and gases with which it has come in contact before and during the ground-water phase of the Hydrologic Cycle (ref. 3). Similarly, the composition of the mud filtrate depends upon the changes that take place as the substances added at the surface react with one another and with the cuttings derived from the formations drilled. When mud filtrate mixes with ground water, reactions may occur to form precipitates which then become subject to the filtration mechanisms listed previously. Factors of Eh and pH, as well as ionic strength, are significant in determining the extent of formation plugging and attendant mineralogical alterations (refs. 28 and 44).

Quartz is the most abundant mineral in sandstone aquifers, the most common type of aquifer. Chemical additives in the mud filtrate may react with the porous media; for example, sodium hydroxide reacts rapidly with the silica in the quartz, especially at elevated temperatures (ref. 24).

Microorganisms, such as bacteria, or enzymes produced by microorganisms, may be present in the ground water or be introduced by the drilling operation, as previously mentioned. Biological activity frequently influences chemical reactions indirectly, and vice versa, by facilitating reactions that lower or raise the pH. Redox processes also may be mediated by bacteria.

The composition, size, and activity of a bacterial population depends on many factors, including (a) temperature, (b) pH, (c) salt content, (d) concentration of nutrients available, (e) types of nutrients available, and (f) oxygen concentration (ref. 20). Because ground water normally contains little dissolved oxygen, and is generally under reducing conditions, anaerobic species are expected to predominate. Bacterial travel in confined aquifers is reportedly negligible and survival time is short. Under most conditions, the restricted travel seems to be the result of the filtering action of the porous medium rather than of "die-off" of organisms. Certain bacteria are generally considered to be responsible for the formation of hydrogen sulfide under certain conditions.

Bacteria are commonly isolated from most oil-field brines. Ground water not associated with deposits of organic matter, however, does not support extensive microbial growth. Hence bacteria carriers are presumed to be clays with associated organic materials.

There are sulphate-reducing bacteria, denitrifying bacteria, methane-producing bacteria, plus a host of other bacteria with uncertain affinities (ref. 17). All may play roles in altering chemical equilibrium of the fluid, as well as formation cement and matrix material.

Of particular importance here is that the variety of organic compounds that can be utilized by microorganisms is almost limitless. Nearly all naturally occurring organic compounds are subject to microbial assimilation, although some, such as humic materials, are attacked very slowly.

In a study on liquid waste-aquifer interactions, Leenheer and Malcolm (ref. 35) explored several of the possible geochemical and biochemical effects of introducing an organic acid into the subsurface environment. After injection, the organic acids were first neutralized by the carbonate minerals in the aquifer. They found evidence for dissolution of the alumino silicate clay minerals by the complexing organic acids. After dilution, conditions become favorable for microbiologic degradation of the organic constituents. Methane is a proposed product with sulfate and iron reduction occurring as byproduct reactions. Figure 9 shows their proposed model of the geobiochemical cell.

Of particular importance in considering the mobility of foreign fluids in an aquifer is that most aquifers exhibit a natural, reducing subsurface geochemical environment (ref. 41). Most aquifers contain extremely low levels of dissolved oxygen. By opening the aquifer via drilling, the reduced condition is replaced by a progressively more oxidizing environment. The initial response to this change is the oxidation of pyrite, or other unoxidized minerals in equilibrium in a reduced environment, which releases ferrous, sulfide, and hydrogen ions into solution. With time, ferric hydroxide precipitates, and the ferrous ion concentration decreases. Several inorganic and microbiological agents have been observed to accelerate pyrite oxidation (ref. 45).

Within many aquifer systems, clays and shales serve as semipermeable membranes, retarding by varying degrees the passage of the dissolved elemental species with respect to water (refs. 25 and 34). The relative retardation by naturally occurring membranes of cations and anions generally present in introduced fluids has been investigated by Kharaka (ref. 33). The conclusion was reached that the retention of these ions depends on the constitution of the membrane and the specific ions involved. The retardation sequences obtained were generally as follows: $Li<Na<NH_3<K<Rb<C_s$ and $Mg<Ca<S_r<Ba$. For anions at higher temperatures the following sequence was developed: $HCO_3<I<SO_4<Cl<Br$.

CONCLUSIONS

After a contaminant enters ground water it may be immobilized by deep filtration; react chemically with components of the interstitial water; react with or be adsorbed on surfaces of the reservoir rock, or be altered through biological activity.

Under normal conditions of the porous medium, the mobility of drilling fluids in the ground-water system is clearly of very limited extent because of a variety of physical, chemical, and biological factors. The very low volume introduced into a very large volume aquifer would further minimize the impact of mobility due to a natural defense against invading carrier fluids involving (a) filtration at and near the well, (b) adsorption over the entire distance of flow, and (c) dilution, increasing away from the well or point source of entry.

It is clear therefore that improved "housekeeping" in surface operations and more effective techniques in controlling "lost circulation" will reduce the chance of point-source contamination of the local ground-water reservoir. Further research, however, is urgently needed to assess the environmental impact of "lost circulation" and related drilling and production phenomena on the ground-water system.

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DISCUSSION

MR. DONALD W. SOLANAS (U.S. Geological Survey, Metairie, Louisiana): I have a comment rather than a question.

In addition to your summation, which I think places it in its proper perspective as to the ground-water contamination, I think it should be remembered by those here who are not familiar with or knowledgeable of the techniques of drilling oil wells, that the ground water and the shallow formations are protected by casings and cemented strings as the well is drilled to deeper depths and as the mud and mud additives are used. This protection also is a plus effect for noncontamination of these valuable ground-water aquifers.

MR. CAMPBELL: I would only add one thing. During the drilling process, lost circulation is an instantaneous thing; it cannot be cased off all that quickly.

Secondly, I think the problem of blowout is far more widespread than we all think. It is just not as dramatic as the previously cited Michigan case (ref. 32) and Bammel field case, and some of the other cases. I think we may have a rather quiet blowout that we may not be aware of--or a "mini blowout," if you will--that may present problems that we are not even aware of with respect to the long-term transmission of drilling fluids or production-related workover fluids that may or may not be toxic.

MR. GEORGE H. HOLLIDAY (Shell Oil Company, Houston, Texas): I would like clarification as to what a "mini blowout" is.

MR. CAMPBELL: You are going to take me to task on that. All right!

MR. HOLLIDAY: Well, I am just concerned, because your summation was good. I thought the gentleman from the USGS made a good point. And I thought that we were on a pretty good wave length and all of a sudden we have developed a new gremlin that has come from the ground, and I would like to hear something more about the gremlin.

MR. CAMPBELL: Okay. Let us talk about the gremlin for a second.

Obviously, I am thinking about the gremlin. Can you imagine a slow pressure release? And can you imagine a nontraumatic blowout where you have just a bleeding, if you will? That is what I was referring to when I mentioned a mini blowout. So let us replace that term--I admit blowout means something more than what I meant--and call it a bleeding of more highly pressurized systems. Post-drilling "lost circulation" is probably a better term.

Now, does that sound like a gremlin?

MR. HOLLIDAY: Yes, as a matter of fact, it does. The conditions which you mentioned I am sure can be conjured. And I think through your thinking process there a minute ago you were able to do this. You recognize that when casing is set and the cement placed in position and let set, we pressure test the casing, drill out below the cement, and again, pressure test. We have done virtually everything that is conceivable and, I think, acceptable as good practice to see that there is not this bleeding operation that you are speaking of.

MR. CAMPBELL: I would say this: I will support you in the fact that generally, industrywide, you do go out of your way, as far as I know, to make sure that the cement is in place and it is holding.

My worry is that with time and with production of that particular oil well, that there may be earth shifting, for instance gravity faulting--I am thinking of the Gulf Plain--which may stress that seal. You do not monitor these wells, unless it becomes a dramatic case of failure and then you have to go back in to rehabilitate that well. My concern here is that, with time and without a monitoring system, there is a significant chance of "bleeding" of "workover" fluids that are similar in character to some drilling fluids. I am not suggesting it is a fact--I need numbers to convince myself it is a problem--and I feel it is something that should not necessarily be made a point of as we are doing here; but let us at least consider it as an area for consideration. If you don't look for areas of potential trouble, you--or the oil industry--will continue to be criticized by outsiders for sweeping potential problems under the rug.

Now, how are we going to monitor it? I do not know. But I do think it could be a problem and deserves serious consideration by your industry.

MR. FORD A. BANKSTON (Union Oil of California, Houston, Texas): I am primarily an operating man and have been in the business since '41. Of the two areas you refer to, let us take drilling first. We now get more exotic, but we used to have a man who watched the mud pits. And when that mud pit starts going down just a little bit or goes up a little bit, we do something drastic.

We have, of course, as the gentleman from the USGS knows, in the more exotic drilling operations, mud tank level indicators that tell us immediately on charts when that mud level goes up or down, and it is not a slow bleed thing.

MR. CAMPBELL: No. You have misconstrued what I said. I am talking about after the well is drilled and in production 5 years later.

MR. BANKSTON: Prior to talking about the production phase, I wanted it understood that your statement about a slow bleed from one zone to another is not likely to happen during drilling operations.

MR. CAMPBELL: I am not talking about bleeding during the drilling operation. I am talking about afterwards, i.e., during production.

MR. BANKSTON: I want to get that clear.

MR. CAMPBELL: I agree with you. You may be right concerning the drilling phase.

MR. BANKSTON: Okay. I am primarily a production man, and you know we keep up with the production from our wells very carefully. If oil production drops off, we check on it, and usually work these wells over. During the workover we would determine if there is channeling in the cement outside the casing or see if we have a hole in the casing. But mind you, most of the fresh-water sands I have worked with have two strings of pipe set through them. That gives quite a lot of protection to the freshwater sands.

What I am really saying is that we have checks on these things; it is not something where a little gremlin can do his dirty work and we do not know that something is happening.

MR. CAMPBELL: I understand your position, but in my opinion, we do not have sufficient data at this time to either discount the problem or call it a gremlin as Mr. Holliday put it. I am sure, however, that your industry will be capable of responding to potentially significant gremlin hunts, if the potential has been defined by either your company's inhouse environmental protection department or by other environmentally cognizant groups. Hopefully, in the near future, both industrial and environmental groups will use the same measuring techniques to assess environmental impact. I suggest that we must work together. The future is approaching....rapidly! Lost circulation of drilling or "workover" fluids, either during the drilling stage or during the production stage, in addition to surface housekeeping has been suggested by us to represent a significant negative impact of well-drilling additives on the ground-water system. We, therefore, urge mutual cooperation in assessing the magnitude of this problem. Thank you.

MOVEMENT OF CHEMICAL CONTAMINANTS IN GROUND WATER

Dean O. Gregg and Keith G. Kennedy*

Abstract

Chemical contaminants in ground water principally move by ground-water flow (convection transport) and by dispersion. In a homogeneous granular aquifer system, the ground-water flow velocities may be reasonably approximated by use of a modification of the Darcy equation. More commonly, however, ground water flows through a locally heterogeneous aquifer of variable permeability with variable gradients and recharge flux. The dispersion (including molecular diffusion) and convection further compound the uncertainties of accurately predicting rates of movement of contaminants in ground water.

The concentration of contaminants in a ground-water system is commonly diluted with distance and time from the source of the contaminants. This dilution, depending on the contaminants, may be due to convection, dispersion, additional recharge, ion exchange, sorption, chemical precipitation, biologial destruction or uptake, and radioactive decay. Some active cations, such as calcium, cesium, sodium, and arsenic, may be removed from solution through ion exchange on clays, silts, and organic material or fixed through sorption. These mechanisms are not significant for a readily dissociated anion, such as chloride or nitrate. Some isotopes of certain chemical species, such as strontium 90, cesium 137, and tritium, exhibit radioactive decay with time, thus reducing their original concentrations.

Examples of movement of chemical contaminants in the ground-water regime are cited. Generally, there is no easy way to perform an investigation of ground-water contamination. As there are so many variables, an extensive data net is usually required.

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INTRODUCTION

The purpose of this paper is to summarize the processes of movement and dilution of chemical contaminants after they have entered the ground-water system from a "point source" and discuss selected recent case histories as examples of these processes.

A common and dramatic example of a point-source ground-water contamination is a complete or partial loss of drilling fluids during exploration or well drilling. Generally, for a partial or complete loss of drilling fluids to occur, two conditions must exist. First, a zone of relatively high permeability must be present. This zone, which typically may be a solution cavity, a highly fractured system, or a highly porous granular material, allows rapid movement of drilling fluid away from the well bore. Second, the formation head in this zone must be significantly lower than the head produced by the column of drilling fluid from that zone to land surface. The resulting head differential produces the drive which forces the drilling fluid into the permeable zone and away from the well bore. The well bore then becomes a point source of aquifer contamination.

After introduction of a drilling fluid or other contamination into the ground-water system, the direction of movement will most likely be radially from the point of injection. However, the extent to which this flow pattern is developed is dependent primarily on the physical properties of the ground-water system. With time and distance, the contamination becomes part of and subject to the dynamics of the existing ground-water regime. The main processes which affect the movement and dilution of chemical contaminants in a ground-water system are discussed below.

MOVEMENT OF CHEMICAL CONTAMINANTS

The two main processes which result in movement of chemical contaminants in ground-water are:

(1) the movement of ground-water itself (convection transport); and

(2) dispersion (including molecular diffusion).

There are other factors in the movement of chemical contaminants in the ground-water regime, but they are generally of less importance and rarely of significance except under special conditions.

Ground-water Movement

Ground-water movement is caused by differences in energy. These differences in energy are mainly due to either differences in elevation or to differences in head or pressure. Basically, water moves from a position of higher elevation or head to a position of lower elevation or head.

The Darcy equation, and modifications thereof, gives the relationship between the physical properties of the system and the rate and quantity of water movement. That is, the quantity of water, Q, moving past a particular place, in a unit of time, is equal to the hydraulic conductivity, K, times the area through which the flow occurs, A, time the difference in head, Δh, divided by the length, ℓ, over which the head drop occurs, or:

$$Q = KA \frac{\Delta h}{\ell} .$$

The hydraulic conductivity of the porous medium, however, depends both upon the nature of the fluid and upon the nature of the media through which the fluid passes. In considering the nature of the fluid, the minor variations in the physical properties of the ground water are commonly ignored. This is because there may be only moderate or low concentrations of dissolved solids and because the temperature of ground water in a particular aquifer is reasonably constant. Thus, the importance of differences in the density and the viscosity of the ground water is negligible. For this reason, a term called intrinsic permeability, k, which depends only on the medium, is commonly used. This term is often shortened to "permeability." In some contamination studies, however, the density and viscosity of the contaminated ground water is significantly different from that of natural ground water. In these instances, the pertinent parameters may be determined and included in the evaluation of the problem.

The rate at which ground water moves through a porous medium can be calculated using a modification of the Darcy equation (the Dupuit-Forchheimer assumption) as follow:

$$V = K \frac{\frac{\Delta h}{\ell}}{n}$$

where n = effective porosity of the medium,
v = ground-water velocity.

The rationale for dividing the right side of the equation by n, the effective porosity, is that flow is occurring through interconnected pore spaces. Thus the actual velocity through the tortuous pathways in the pores of the medium may be considerably greater than the apparent flow velocity through the water-bearing zone.

In a granular porous medium, such as a sand or gravel, the direction and rate of ground-water movement may be predicted with some degree of certainty. Commonly, however, flow takes place in heterogeneous systems such as fractured or solution-cavity-riddled rocks or in rocks of highly variable permeability. The determination of flow velocities through these aquifers is more difficult and prediction less certain than for the granular system.

Convective transport, as used here, results from the mechanical mixing of the contaminant with uncontaminated ground water and the resultant movement with the ground water. The degree to which the mixing occurs and the overall rate of convective transport is a function of the ground-water pathways in the porous medium.

Dispersion

Dispersion results from convection and diffusion (the random movement of molecules caused by thermal and kinetic energy). The dispersion coefficient is a function of the velocity of ground-water movement, of the effective porosity of the aquifer and of the molecular diffusion of the fluid. The dispersion phenomena may account for the presence of contaminants in locations different than that of the ground-water flow direction.

DILUTION OF CHEMICAL CONTAMINANTS

Physical, biologic, and geochemical processes are responsible for dilution of contaminated ground water depending on the particular hydrogeologic environment and the nature of the contaminant(s). The term "dilution" is used broadly to imply a lowering of concentration of any particular chemical constituent with time and distance from the point source and includes the mechanisms or removal and conversion of the constituents.

Physical Processes

The physical processes which result in dilution of contaminated ground water are:

(1) convective transport; and
(2) dispersion (including molecular diffusion).

These two processes, as were discussed above in conjunction with recharge of contaminated ground water to the affected zone, represent the main effective physical dilution phenomena. The recharge is generally most effective in situations where contamination of a water-table aquifer has occurred and the downward movement of uncontaminated water results in a volumetric dilution, in dispersion, and in a potential from convective transport.

Biological Processes

Biologic processes which result in dilution of ground-water contamination are:

(1) By green plant uptake of contaminants from the shallow ground water; and

(2) by bacterial action.

The green plants take up, and therefore remove, contaminants from the soil or shallow ground water. The importance of green plant-related biological processes is generally less significant compared to the bacterial processes in causing dilution. Bacteria have been shown to cause dilution by decomposing injected organic wastes (refs. 1,2) and in other studies have been shown to ingest and remove a variety of other potential contaminants.

Geochemical Processes

The main geochemical processes which may result in dilution of ground-water contamination are:

(1) ion exchange;
(2) sorption (fixation);
(3) chemical precipitation; and
(4) radioactive decay.

Ion exchange is defined as "the exchange of an ion held by electrical charge near the surface of an exchange mineral with an ion present in solution in which the exchange mineral is immersed" (ref. 3). Ion exchange is a dynamic process dependent on the nature of the source of ionic charge sites, the chemical composition of ground-water solution, the proportion of monovalent versus multivalent cations, and the pH. The precise course of an exchange reaction can vary significantly as these characteristics are altered.

Most ion exchange reactions involve cations, although examples of anion exchange are cited in the literature and further research is being carried on in this field. (Anion exchange capacity may be important where kaolinite and hydroxides of iron and aluminum are present). Many natural minerals have exchange capacity although clay minerals, particularly the montmorillonite group, are the most effective. The organic matter in soil materials can also provide significant exchange capacity. Therefore, in instances where ground water is moving through media containing clay minerals or decomposed organic matter (humus), ion exchange mechanisms may be very effective in altering the chemical nature of the ground water. Perhaps one of the most common ion exchange examples is the exchange of Ca^{++} and Mg^{++} in water to mineral sites for Na^{+} and K^{+} released to the ground water. The exchange of Ca^{++} or Mg^{++} for H^{+} is an important phenomenon where acidic conditions prevail.

Sorption (fixation) causes removal of ions from solution by fixation within the crystal lattice of a mineral. The capacity for this type of reaction is dependent on the nature of the minerals present and is a result of direct chemical bonding of unsatisfied charges within the mineral structure. An example is the fixation (sorption) of potassium within the lattice of illitic clays which have lost K^{+} ions through previous weathering. Completion of the crystal lattice often results in stabilization of the physical structure of a mineral such that this sorption process may be viewed in part as a physical as well as a chemical phenomena.

Chemical precipitates cause dilution by combining elements as the result of the mixing of ground waters which have differing chemistry, temperature, and in rare instances, pressure. Precipitation related to contamination studies has been intensively studied most recently in areas of mine surface-water drainage. In instances where the pH and temperature of two mixing solutions differ, precipitation of certian constituents may also result in removal of contaminants from the ground water. In the zone of aeration, oxidation of certain dissolved substances such as iron may cause precipitation. Detailed studies are needed in areas where oxidation of contaminated ground water may result in the formation of potentially hazardous precipitates.

Radioactive decay causes dilution by the material disintegration of iostopes. Some of this disintegration may constitute an environmental hazard. The potential effects of the accidental introduction of radioactive materials to the ground-water system should be anticipated and evaluated prior to the construction of any facility handling these materials. Simulation by computer models may be used to evaluate the potential hazard of such an accidental introduction of radioactive materials using the physical parameters of the media and the chemical processes of contaminant movement and dilution as referred to above (including radioactive decay). Most attention is focused upon isotopes tritium (H-3), strontium (Sr-90), and cesium (Cs-137). The methods of making an appraisal of the potential hazard of radioactive contamination are becoming increasingly more sophisticated as the necessity of assuring the safety of the environment is realized.

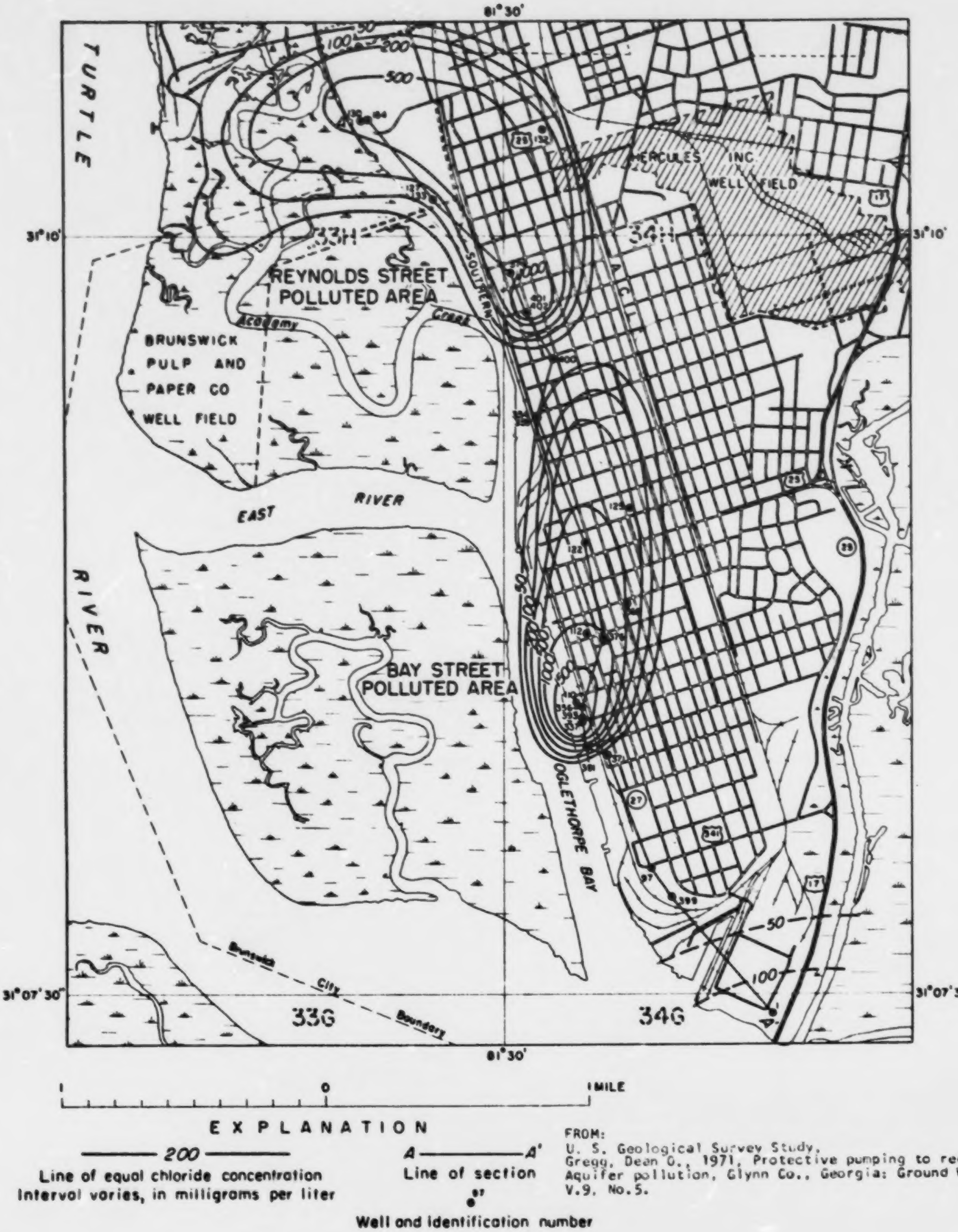
CASE HISTORIES

Several examples are cited in the following paragraphs to illustrate the variability of movement and dilution of chemical contaminants in a ground-water system.

Chloride Contamination, Brunswick and Glynn County, Georgia

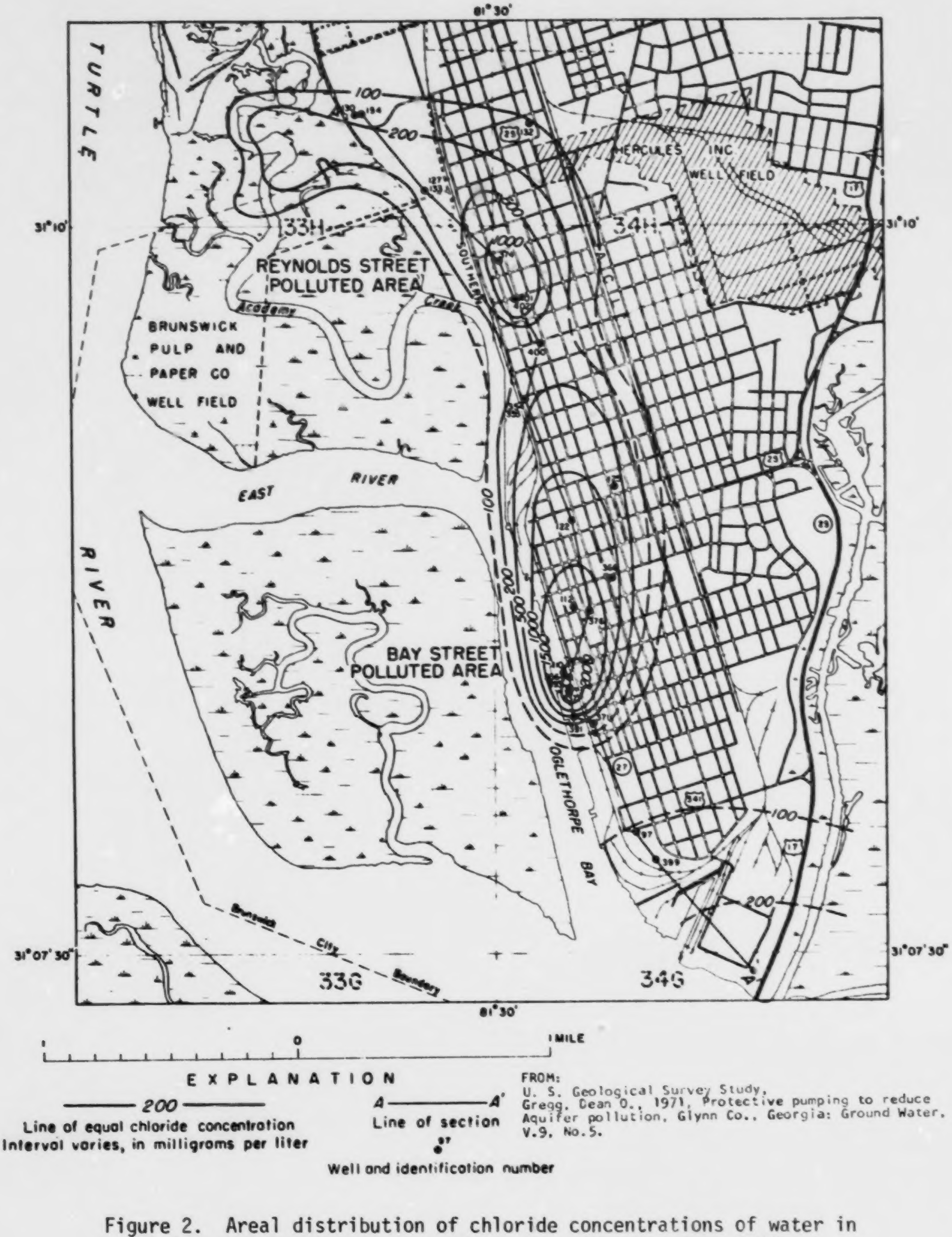
Contamination of the principal artesian limestone aquifer by brackish water has occurred in places in and near Brunswick, Georgia. The U.S. Geological Survey conducted comprehensive investigations to determine the geohydrologic controls of this contamination, and concluded (ref. 4) that man's withdrawal of freshwater from the upper and lower water-bearing zones of the principal artesian aquifer has created a head imbalance with brackish ground water. This head imbalance or potential has created conditions favorable for the deep brackish water to migrate to the shallower freshwater zones of lower hydraulic head. Joints, fractures, faults, or solution openings, and, in several instances, uncased wells, are the probable vertical conduits for the migration of this brackish water across confining zones to the freshwater zones.

Figures 1 and 2 (ref. 5, plate 6) show the distribution of chloride concentrations in two different aquifer zones from three known areas of contamination in Brunswick, Georgia. The point source of contamination evident in the southeast corner of these maps is probably related to well no. 1. This well was drilled through the lower confining unit separating the lowest of two water-bearing zones (fresh) from the underlying brackish-water zone (ref. 6). This unused well forms a vertical


81°30'
31°10'
31°07'30"
TURTLE RIVER
EAST RIVER
REYNOLDS STREET POLLUTED AREA
BAY STREET POLLUTED AREA
BRUNSWICK PULP AND PAPER CO WELL FIELD
HERCULES INC. WELL FIELD
Academy Creek
SOUTHERN
A.C.L.
OGLETHORPE BAY
Brunswick City Boundary
33H
34H
33G
34G
50
100
200
500
1000
2000
25
17
27
341
A
A'
1
0
1 MILE
EXPLANATION
200
Line of equal chloride concentration Interval varies, in milligrams per liter
A A'
Line of section
97
Well and identification number

FROM:
U. S. Geological Survey Study,
Gregg, Dean O., 1971, Protective pumping to reduce Aquifer pollution, Glynn Co., Georgia: Ground Water, V.9, No.5.

Figure 1. Areal distribution of chloride concentrations of water in the upper water-bearing zone, Brunswick, Georgia, June 1969.


81°30'
TURTLE
RIVER
100
200
HERCULES INC
WELL FIELD
31°10'
33H
34H
1000
SOUTHERN
REYNOLDS STREET
POLLUTED AREA
Academy Creek
BRUNSWICK
PULP AND
PAPER CO
WELL FIELD
400
EAST RIVER
100
200
500
1000
1500
BAY STREET
POLLUTED AREA
OGLETHORPE BAY
23
25
17
27
341
100
200
Brunswick City Boundary
31°07'30"
33G
34G
A
A'
81°30'
1
0
1 MILE
EXPLANATION
200
Line of equal chloride concentration
Interval varies, in milligrams per liter
A
A'
Line of section
97
Well and identification number

FROM:
U. S. Geological Survey Study,
Gregg, Dean O., 1971, Protective pumping to reduce Aquifer pollution, Glynn Co., Georgia: Ground Water, V.9, No.5.

Figure 2. Areal distribution of chloride concentrations of water in the lower water-bearing zone, Brunswick, Georgia, June 1969.

conduit allowing the higher-head brackish water to move up the well bore and into the upper and lower water-bearing zones. A similar situation exists at both the Bay Street and the Reynolds Street contaminated areas. Here the vertical conduit is not identified, but it is likely a natural joint, fracture, fault, or solution opening.

Industrial pumping controls the configuration of the potentiometric surface and controls the direction of movement of ground water in Brunswick-Glynn County area. The lines of equal chloride concentration are oriented along flow paths from the point source of contamination toward the well field at the Brunswick Pulp and Paper Company (figs. 1 and 2). The ground-water movement is about 350 feet a year (ref. 5).

The width of the body of chloride contamination may have been accentuated due to the inhomogenity of the solution-openings in the limestone, to lateral pumping effects, to dispersion, and to convection transport. Harlan B. Counts, Hydrologist with the U.S. Geological Survey, reports (oral communication, May 14, 1975) that the traverse dispersion coefficient is about 30 percent of the lateral dispersion coefficient.

The chloride contamination problem in the Brunswick-Glynn County area illustrates the process of induced leaking, and of the movement and distribution of contaminates within the ground-water system. The identification of this problem has been very time-consuming and expensive but the techniques used and the concepts developed during this study have been proved to be applicable to similar problems elsewhere.

Chloride and Arsenic Contamination, Wisconsin

Dames & Moore recently performed an extensive investigation of chloride and arsenic contamination of ground and surface water at a site in Wisconsin. The contamination occurred through long-term leaching of stockpiles of waste salt into the ground-water system, and hence into a nearby river. The site is underlain by about 40 feet of predominately silty sands, cohesive clayey silts, and gravels, all of which contain some organic material. Underlying these fluvial deposits is a dolomite bedrock which constitutes an aquifer in the area.

A plot plan of the site, showing the stockpiles of the salt waste, the data points used in this study, and the section lines are shown in figure 3. Cross sections for the site (figs. 4 and 5) are annotated with the permeability values and with the chloride and arsenic concentrations associated with the control points. Not all of the data control points are shown on these sections, as some water quality information is interpreted from off-section data. Figure 6 shows the horizontal distribution of chloride values in the 20- to 30-foot zone.

As evidenced by figures 4 and 5, several silts and clayey silts were present at the site. However, these units are discontinuous and do not protect the underlying bedrock from chloride and arsenic contamination. The head of the ground water in the dolomite bedrock is higher than the head of the ground water in the surficial fluvial material. This effectively prevents contamination of the dolomite bedrock.

Brines containing extremely high concentrations of chloride, arsenic, sulfate, sodium, and other constitutents are collecting beneath the main salt-waste storage pile. With total dissolved solid levels up to 158,600 mg/l, the specific gravity is more than 1.1 mg/ml. Thus the brines, being heavy, sink in the shallow aquifer. Because the aquifer permeability and the hyradulic gradients are low, the brines are not being appreciably flushed from the aquifer.

The arsenic ion, because of its attraction to the silts, clays, and organic soil particles, moves very slowly through the ground-water system. This was established by performing sorption and leaching tests in the laboratory and by analysis of field data. Conversely, the chloride ions dissociate and disperse readily. These two differing phenomena result in an apparent decrease in arsenic ions with respect to chloride ions with distance from the source areas. Sodium also decreases with respect to the chloride ions with distance. In actuality, the arsenic ion is probably in the form of an arsenate, an anion, thus the arsenic must also be in a complex with some other cation to be so readily attracted to the clays, silts, and organic material.

The discharge of contaminated ground water to the river was found to be about 3,000 gallons per day. This low rate of discharge may be

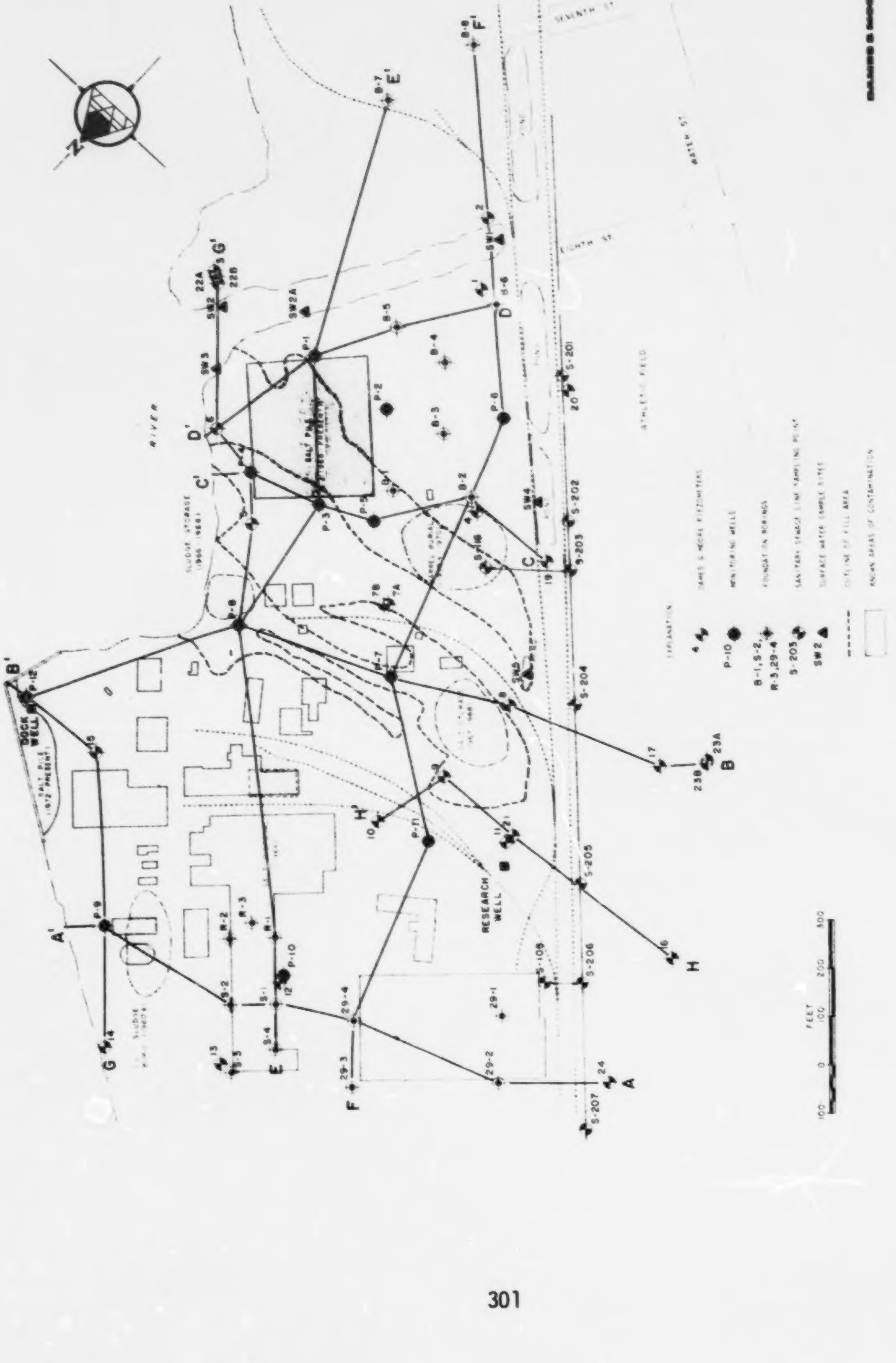
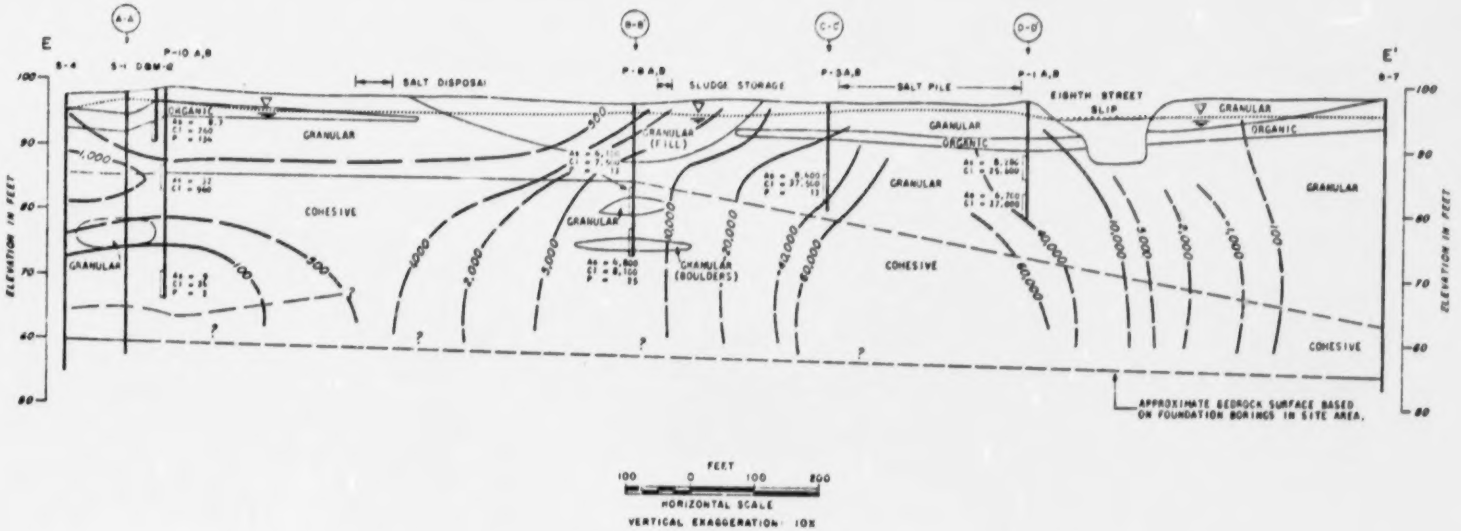

RIVER
DOCK WELL
RESEARCH WELL
SLUDGE STORAGE (1966-1968)
ATHLETIC FIELD
SEVENTH ST.
EIGHTH ST.
WATER ST.
A A' B B' C C' D D' E E' F F' G G' H H'
EXPLANATION
DAMES & MOORE PIEZOMETERS
P-10 MONITORING WELLS
B-1, S-2, R-3, 29-4 FOUNDATION BORINGS
S-205 SANITARY SEWAGE LINE SAMPLING POINT
SW2 SURFACE WATER SAMPLE SITES
OUTLINE OF FILL AREA
KNOWN AREAS OF CONTAMINATION
FEET
100 0 100 200 300

Figure 3. Plot plan of data points and sources of contamination.


E
E'
A-A'
B-B'
C-C'
D-D'
B-4
S-1
DBM-2
P-10 A,B
P-8 A,B
P-3A,B
P-1 A,B
B-7
SALT DISPOSAL
SLUDGE STORAGE
SALT PILE
EIGHTH STREET SLIP
ORGANIC
GRANULAR
COHESIVE
GRANULAR (FILL)
GRANULAR (BOULDERS)
As = 8.7
Cl = 260
P = 134
As = 22
Cl = 960
As = 2
Cl = 36
P = 3
As = 6,100
Cl = 7,500
P = 13
As = 6,800
Cl = 8,100
P = 35
As = 8,400
Cl = 37,500
P = 13
As = 8,106
Cl = 25,600
As = 6,700
Cl = 37,000
100
500
1,000
2,000
5,000
10,000
20,000
40,000
60,000
?
APPROXIMATE BEDROCK SURFACE BASED ON FOUNDATION BORINGS IN SITE AREA.
ELEVATION IN FEET
100
90
80
70
60
50
FEET
100
0
100
200
HORIZONTAL SCALE
VERTICAL EXAGGERATION: 10X

KEY:

As - TOTAL ARSENIC (mg/l)

Cl - CHLORIDE (mg/l)

P - PERMEABILITY (TO NEAREST gpd/ft²)

EFFECTIVE INTERVAL OF PIEZOMETER

(A-A') LOCATION OF OTHER CROSS-SECTIONS

·············· WATER TABLE

GRANULAR - SOILS CONSISTING GENERALLY OF CLEAN SAND AND GRAVELS, SILTY SANDS AND GRAVELS, ORGANIC SANDS AND GRAVELS, LAYERED SANDS AND GRAVELS.

ORGANIC - SOILS CONSISTING GENERALLY OF PEAT OR HUMUS, SANDY ORGANIC SOILS, SILTY AND GRAVELLY ORGANIC SOILS, AND CLAYEY AND GRAVELLY ORGANIC SOILS.

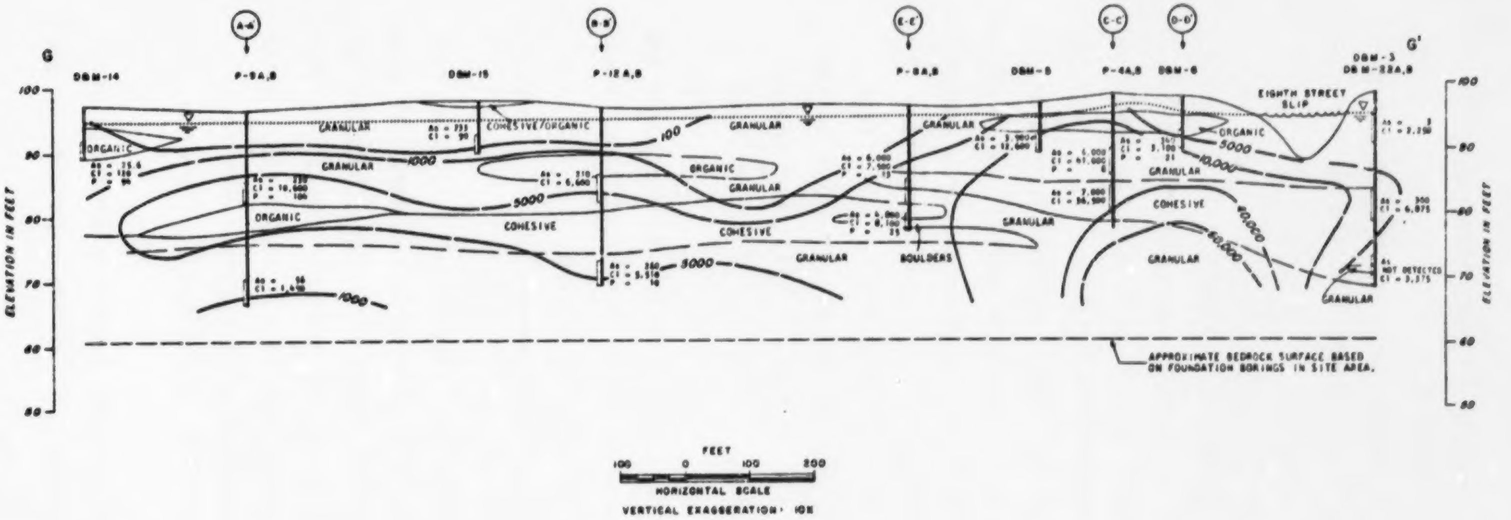
COHESIVE - SOILS CONSISTING GENERALLY OF CLAYS AND SILTS WITH MINOR AMOUNTS OF OTHER CONSTITUENT SOIL TYPES.

NOTES:

1. ALL ELEVATIONS RELATIVE TO PLANT DATUM.
2. RIVER WATER LEVEL MEASURED JANUARY, 1975 AS ≃95.1 FEET.
3. LITHOLOGY CONTACTS ARE AS SHOWN WITH SOLID LINES. IN AREAS WHERE LIMITED DATA IS AVAILABLE, DASHED LINES SHOW INFERRED CONTACTS BASED ON AVAILABLE DATA.
4. CHLORIDE CONTOURS ARE BASED ON VALUES FROM PIEZOMETERS AND ARE SHOWN AS DASHED LINES WHERE DATA IS NOT AVAILABLE.

DAMES & MOORE

Figure 4. Generalized subsurface section E-E'.


G
G'
A-A'
B-B'
E-E'
C-C'
D-D'
DBM-14
P-9A,B
DBM-15
P-12A,B
P-8A,B
DBM-5
P-4A,B
DBM-6
DBM-3
DBM-22A,B
ELEVATION IN FEET
100
90
80
70
60
50
GRANULAR
ORGANIC
COHESIVE/ORGANIC
COHESIVE
BOULDERS
EIGHTH STREET SLIP
100
1000
5000
10,000
40,000
60,000
As = 75.6
Cl = 120
P = 90
As = 230
Cl = 10,600
P = 100
As = 56
Cl = 1,490
As = 735
Cl = 90
As = 210
Cl = 6,600
As = 260
Cl = 5,510
P = 10
As = 6,000
Cl = 7,500
P = 13
As = 6,000
Cl = 8,100
P = 25
As = 3,900
Cl = 12,600
As = 5,000
Cl = 41,000
P = 6
As = 7,000
Cl = 56,500
As = 347
Cl = 3,100
P = 21
As = 3
Cl = 2,250
As = 300
Cl = 6,875
As NOT DETECTED
Cl = 3,375
APPROXIMATE BEDROCK SURFACE BASED ON FOUNDATION BORINGS IN SITE AREA.
FEET
100
0
100
200
HORIZONTAL SCALE
VERTICAL EXAGGERATION: 10X

KEY:

As - TOTAL ARSENIC (mg/l)

Cl - CHLORIDE (mg/l)

P - PERMEABILITY (TO NEAREST gpd/ft^2)

EFFECTIVE INTERVAL OF PIEZOMETER

(A-A') LOCATION OF OTHER CROSS-SECTIONS

WATER TABLE

GRANULAR - SOILS CONSISTING GENERALLY OF CLEAN SAND AND GRAVELS, SILTY SANDS AND GRAVELS, ORGANIC SANDS AND GRAVELS, LAYERED SANDS AND GRAVELS.

ORGANIC - SOILS CONSISTING GENERALLY OF PEAT OR HUMUS, SANDY ORGANIC SOILS, SILTY AND GRAVELLY ORGANIC SOILS, AND CLAYEY AND GRAVELLY ORGANIC SOILS.

COHESIVE - SOILS CONSISTING GENERALLY OF CLAYS AND SILTS WITH MINOR AMOUNTS OF OTHER CONSTITUENT SOIL TYPES.

NOTES:

1. ALL ELEVATIONS RELATIVE TO PLANT DATUM.
2. RIVER WATER LEVEL MEASURED JANUARY, 1975 AS ≃95.1 FEET.
3. LITHOLOGY CONTACTS ARE AS SHOWN WITH SOLID LINES. IN AREAS WHERE LIMITED DATA IS AVAILABLE, DASHED LINES SHOW INFERRED CONTACTS BASED ON AVAILABLE DATA.
4. CHLORIDE CONTOURS ARE BASED ON VALUES FROM PIEZOMETERS AND ARE SHOWN AS DASHED LINES WHERE DATA IS NOT AVAILABLE.

DAMES & MOORE

Figure 5. Generalized subsurface section G-G'.

attributed to the configuration and gradient of the water table and to the low permeability of the surficial material.

The results of this investigation showed that the contamination is localized and is not a substantial environmental hazard to the area.

Cyanide and Other Buried Toxic Wastes--Illinois

A similar study involving toxic wastes was conducted in Illinois. Our client purchased farm acreage for a right-of-way. Shortly after purchase, three cattle owned by a tenant farmer died in an intermittent creek bed supposedly after drinking water from puddles. The cattle and the puddles were down gradient from about 1,500 partially buried drums and barrels, some of which contained toxic chemical wastes. This chemical waste, which includes cyanides, chromium, cadmium, nickel, copper, lead, zinc, and phenols, had been disposed of in side-hill gullies in a limestone terrain prior to the purchase of the land by the client. Dames & Moore was retained to identify the nature and location of the source; to determine the extent of contamination of soil, and ground and surface water; and, most importantly, to evaluate the threat of contamination to the ground-water users in the area.

The three cows which had died and had been buried were exhumed and samples of blood, liver, and lung tissue analyzed for cyanide and selected heavy metals. A veterinarian toxicologist evaluated the tissues and the laboratory analyses and indicated that, in his opinion, death was induced by cyanide.

In the course of the investigation, soil samples at 2-foot intervals to a maximum depth of 6 feet from more than 50 sites were collected and analyzed for cyanide. These analyses showed generally that the cyanide concentration decreases with depth and is commonly "held" in the silts, clays, and organic material, and is not "held" as tightly in the granular material. Significant concentrations of cyanide were found in soil samples from the mouth of the creek, more than a mile from the disposal area.

The concentrations of contaminants in the ground water contained in limestone have been found to be erratic. It varies depending in part upon precipitation, which controls the leaching and deposition of cyanide and selected heavy metals from the source areas to the soils and to the ground-water regime. Shortly after the spring thaw in the soil zone and the percolation of spring rains to the water table, a substantial increase in cyanide and heavy metals was detected in the ground water. A few weeks later, the concentrations of chemicals had decreased to lower levels. Many domestic wells in the area have been condemned by the State and are not being used for human consumption. The residents are hauling drinking water.

The chemical waste disposal areas in the side-hill gullies, fortunately, are generally ground-water discharge areas, depending on the time of year and the water levels. Precipitation following an extended drought can locally and temporarily alter the ground-water flow patterns and the side-hill areas may recharge the system for a period of time.

The intermittent flows of surface water, when present, usually have relatively high concentrations of cyanide and heavy metals. The concentration of chemicals in the surface-water runoff typically decreases with distance from the source areas. This is due to dilution from uncontaminated ground-water inflow, oxidation and destruction of cyanide, and precipitation of certain constituents.

RADIOCHEMICAL CONTAMINATION CALCULATIONS

Another investigation conducted by Dames & Moore was concerned with the postulated accidental release of approximately 950 gallons of radioactive waste to a ground-water system. The shallow ground-water system eventually discharges to a nearby lake. Hydrodynamic dispersion, fluid concentration, cation exchange, and radionuclide decay were considered in the evaluation of postulated radioactive contamination of the lake.

Figure 6 shows the hydrologic setting of the site. The hypothetical release point for the 950 gallons of radioactive effluent lies partially buried on the nose of a hill 600 feet from and about 15 feet above the lake. As expected, the natural ground-water gradient is

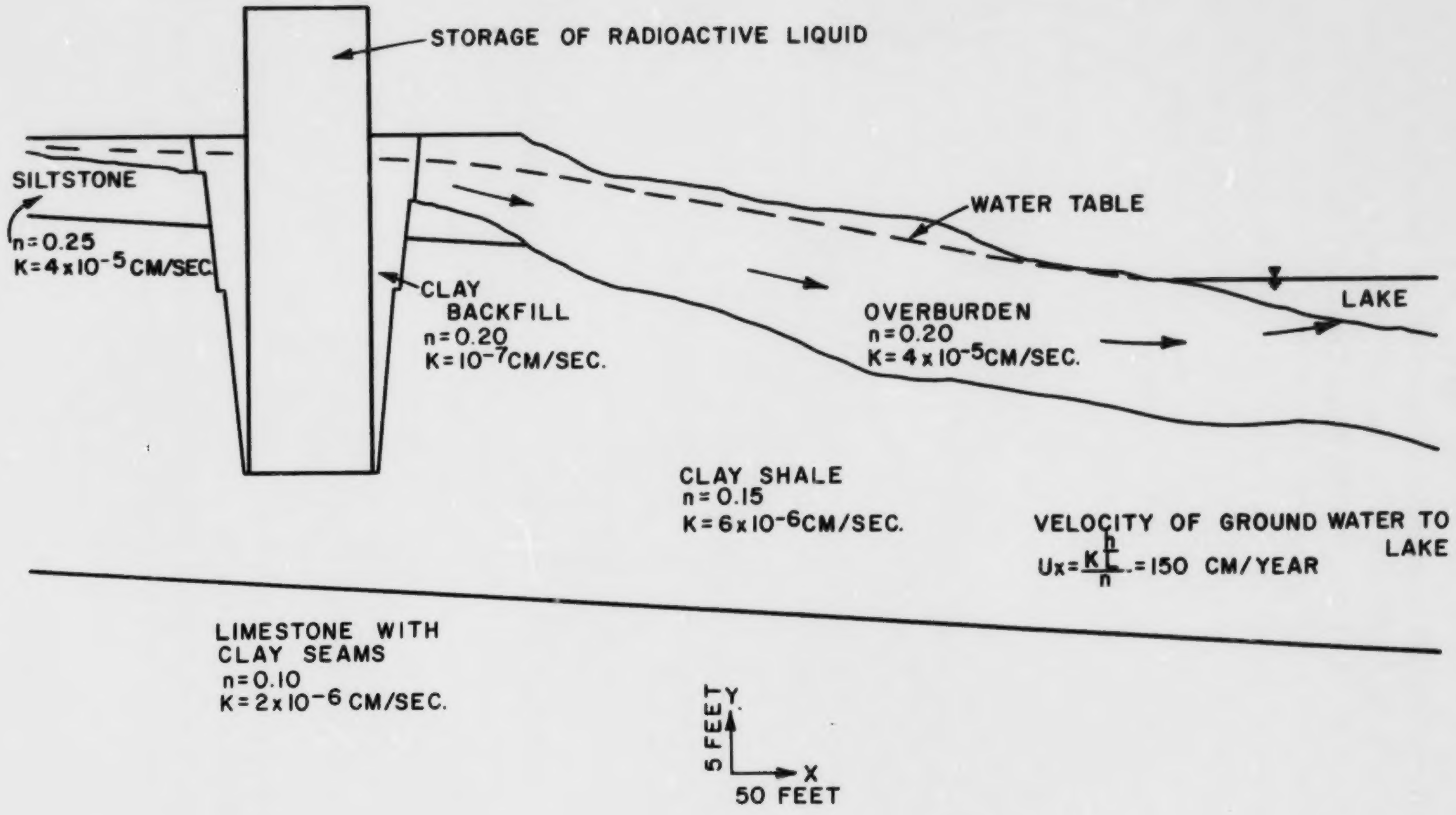

STORAGE OF RADIOACTIVE LIQUID
SILTSTONE
n=0.25
K=4x10-5 CM/SEC
WATER TABLE
CLAY BACKFILL
n=0.20
K=10-7CM/SEC.
OVERBURDEN
n=0.20
K=4x10-5CM/SEC.
LAKE
CLAY SHALE
n=0.15
K=6x10-6CM/SEC.
VELOCITY OF GROUND WATER TO LAKE
Ux=K(h/L)/n=150 CM/YEAR
LIMESTONE WITH CLAY SEAMS
n=0.10
K=2x10-6 CM/SEC.
5 FEET
Y
X
50 FEET

Figure 6. Generalized geology and groundwater flow.

toward the lake at about 0.02 foot per foot. The lithology, porosity, and permeability of the various units at the site are indicated on the cross section (fig. 6).

An equation describing the dispersion and attenuation of a contaminating liquid introduced instantaneously as a finite cuboid volume into the ground-water system was derived by integration of the Baetsle and Souffriau equation (ref. 7). The result, which is similar in form to the Lenda and Zuber analytic model (ref. 8), accounts for the total quality of radionuclides introduced with the effluent slug, radioactive decay, average pore-water velocity, cation exchange, and dispersion of contaminants in the ground water.

Table 1 summarizes the conservatively developed input parameters used in the analytic model. Only Cs-137 and Sr-90 isotopes were considered in this problem because the other possible constituents have much shorter half-lives relative to the long ground-water travel times.

Table 1. Summary of input parameters

Input Parameter	Material Property	CS-137	Sr-90
Cation exchange capacity, (meq/gm)		0.061	0.029
Equilibrium exchange constant with Ca		29.0	0.81
Concentration of calcium in interstitial fluids, C_{Ca} (meq/ml)	0.0465		
Flux rate, (cm/yr)	29.148		
Dispersion coefficient, (cm^2/yr)	322		
Length of travel path (cm)	18,288		
Porosity of unit	0.20		
Bulk density, (g/cm^3)	2.00		
Cuboid size per side, (cm)	262.8		
Half-life, (yr)		33	29

The travel times for the maximum concentration front to enter the lake were calculated, using the finite effluent slug model described above, as 48,000 years and 800 years for Cs-137 and Sr-90, respectively. It was concluded that radionuclides entering the lake as a result of the postulated accident would not pose an environmental hazard to the lake.

SUMMARY

The movement and dilution of chemical contaminants in a ground-water system are mainly controlled by the physical processes of convection transport and dispersion; by the geochemical processes of ion exchange, sorption, precipitation, and, in some cases, radionuclide decay; and biological processes. The discussion of several case histories illustrates the effects of the variability of the ground-water system and the properties of the fluid on the movement and dilution of chemical contaminants. The most common feature of these cited investigations was the use of appreciable amounts of data. Only with sufficient amounts of the appropriate types of data can an investigation of contamination on ground water be accurately made. Generally, there are few, if any, easy ways to determine the vertical and lateral extent, the rate and direction of movement, and the dilution of ground-water contamination in many ground-water systems.

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TOXICITY AND ENVIRONMENTAL PROPERTIES OF CHEMICALS USED IN WELL-DRILLING OPERATIONS

Vladimir Zitko*

Abstract

Acute toxicity to fish and other environmental effects of drilling mud components are discussed. The components include solids, particularly barite, polymers, and low molecular weight organic compounds. Acute toxicities in terms of 96hLC0 (juvenile Atlantic salmon, Salmo salar) were estimated for a number of organic components of drilling mud on the basis of correlations with octanol-water partition coefficients and Hammett σ constants. The components include 4- and other substituted 1,2-dihydroxybenzenes, benzoic acids, and naphthalenes. Acute toxicity of several substituted imidazolines and sodium petroleum sulfonates is reported.

It is concluded that the most pronounced environmental effects of drilling mud may be due to physical action of suspended solids. Organic additives may possibly be selected in such a way that the use of highly toxic compounds will be eliminated.

INTRODUCTION

In comparison with studies of the environmental effects of petroleum, very little attention was given to the toxicity and environmental properties of materials used in well-drilling operations. Simpson reviewed the state-of-the-art in mud engineering, paying particular attention to chromolignite, chromolignosulfonate, and surfactants (ref. 1). Collins discussed the pollution potential of petroleum production; presented a list of components of drilling muds, well-treatment chemicals, and brines; and indicated the consumption of some of the chemicals (ref. 2). Falk and Lawrence determined the acute toxicity of drilling muds and some

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of their components, as used in the Canadian Arctic. The 96hLC50 values for fish ranged from 0.8 to 12 percent for drilling muds and 22 to 81 percent for sumps (ref. 3). The authors suggested establishing toxicity limits for the effluents and regulating the concentration of hydrocarbons and suspended solids, pH, BOD, and COD. Land reviewed recently the toxicity of drilling mud components (ref. 4).

This paper discusses the acute toxicity and some environmental properties of drilling mud components and chemicals used in well-drilling operations. Particular attention is given to organic additives. The acute toxicity of some of the compounds was determined, and structure-activity relationships were used to estimate the toxicity of others.

INORGANIC COMPONENTS

Barite and clays are the main suspended solids in drilling muds (refs. 4,5). Barite particles are quite small (-325 mesh) and it has been estimated that approximately 110 lb/1,000 t is lost to the atmosphere as a result of handling (ref. 6). No data on the amounts discharged in water are available. The annual consumption of barite in the United States probably exceeds 1.2×10^6 t/year (ref. 6).

The background concentration of barium in seawater is 0.03 mg/l (ref. 7). As a result of barite discharges, the concentration of barium may be significantly increased in localized areas. The solubility of barite in seawater and freshwater, expressed as barium, is 14.8 and 3.6 mg/l, respectively. The increased levels of dissolved barium are probably not environmentally significant since barium has a relatively low toxicity in comparison with other metals.

Using the data of Baudouin and Scoppa (ref. 8), the acute toxicity of a number of divalent cations to three species of aquatic fauna was correlated with the cation binding constants of glycine in equations (1) to (3).

$$\log c = -0.627 \log K_1 + 1.26 \qquad (1)$$

$$\log c = -0.419 \log K_1 + 1.13 \qquad (2)$$

$$\log c = -0.381 \log K_1 + 1.44 \qquad (3)$$

where c = 48hLC50 in millimoles/l,

K_1 = cation binding constant of glycine.

Equations (1), (2), (3) apply to *Daphnia hyalina, Eudiaptomus padanus padanus*, and *Cyclops abyssorum prealpinus*, respectively. The values of log K_1 are 0.77, 0.91, and 8.3 for barium, strontium, and copper, respectively. It can be seen that the acutely toxic concentration of barium, which was not determined by Baudouin and Scoppa, should be in the neighbourhood of 500 mg/l.

Barite and other suspended components of drilling mud would affect the environment physically. For example, the pumping rate of oysters is depressed 50 percent in the presence of suspended matter at 100 mg/l (ref. 9), and the uptake of calcium by clams and seaweeds is decreased to 50 percent of the normal level in the presence of 6.5 and 0.4-0.8 percent of suspended solids (ref. 10). Suspended solids are deleterious to bottom-dwelling organisms when the bottom is covered by a 1-cm layer of fine solids. The plankton abundance is reduced 22 percent by sedimenting suspended matter at a concentration of 250 mg/l, and no plankton can be found in the presence of 2 percent of suspended solids (ref. 10). On the other hand, fish are apparently attracted by high concentrations of drilling muds (ref. 11).

The physical effects of suspended solids may be minimized by a good dispersion, and Mackin and Hopkins concluded that barite had no effect on the survival of oysters (ref. 12).

The baseline levels of suspended solids are relatively low. A concentration of up to 500 mg/l may be encountered in river runoffs, but normally the levels are approximately 30 mg/l and the solids contain about 33 percent of organic material. Near-shore levels of suspended material are of the order of a few mg/l and decrease within a relatively short distance to 0.1 mg/l (ref. 13). The concentration of suspended solids in the open ocean ranges from 0.03 to 0.07 mg/l (ref. 14).

Chromium is another important constituent of drilling muds. In chromolignosulfonates and very likely in the presence of any appreciable amount of organic matter, chromium is present in its trivalent form (ref. 15), and bound quite strongly to organic matter, as it was demonstrated in the case of chromolignosulfonates (ref. 16). The binding of chromium by organic matter may make chromium unavailable to aquatic fauna and flora and significantly reduce its toxicity. In the absence of organic matter, chromium is highly toxic, at least to certain species. The reported ranges of toxicity in terms of 48- or 96hLC50 are 0.01-76, and 0.05-133 mg/l for tri- and hexavalent chromium, respectively (ref. 17).

Arsenite is used as a corrosion inhibitor (ref. 2). The acute toxicity of arsenite is in the order of 1-2 mg/l (ref. 18). Quite high background levels of arsenic, presumably of natural origin, may be found in shellfish.

Many aquatic and particularly marine species are very sensitive to pH. Clam and oyster embryos survived in a pH range of 7.00-8.75 (ref. 19). Values of pH<8 were on the other hand lethal to herring. (ref. 20).

POLYMERS

A number of polymers--natural, modified natural, or synthetic--may be used in drilling muds. These compounds are generally nontoxic due to their high molecular weight, which prevents them from entering living cells. On the other hand, residual monomers, oligomers of relatively low molecular weight, or residues of modifying chemicals (such as long-chain aliphatic amines, which are used to treat some lignosulfonates) could be appreciably toxic.

Polysaccharide-based materials are probably readily biodegraded, but lignites, lignosulfonates, and humic acids are very stable and so are some synthetic polymers.

In the case of lignosulfonates, the biodegradability depends on the source of the material, and kraft-derived lignosulfonates are much more readily biodegraded than the true lignosulfonates, originating in the sulfite process (ref. 21). The biodegradability of wood fiber decreases with increasing lignin content, and ground wood (mechanical pulp) hardly undergoes any degradation (ref. 22).

An ethylene-maleic acid copolymer was not biodegraded over a period of 30 days, whereas, in the same time, 7 and 20 percent of sodium polyacrylate and a methyl vinyl ether-maleic acid copolymer, respectively, were degraded (ref. 23).

LOW MOLECULAR WEIGHT ORGANIC COMPOUNDS

The reviews mentioned earlier, an EPA list of chemicals used in well drilling, and a search of recent patent literature indicates a number of low molecular weight organic additives for use in drilling muds. Toxicity data are not available for most of these compounds, and the following attempts to estimate their acute toxicity from structure-activity relationships are derived from our studies of the general relationships between the acute toxicity and structure of chemicals.

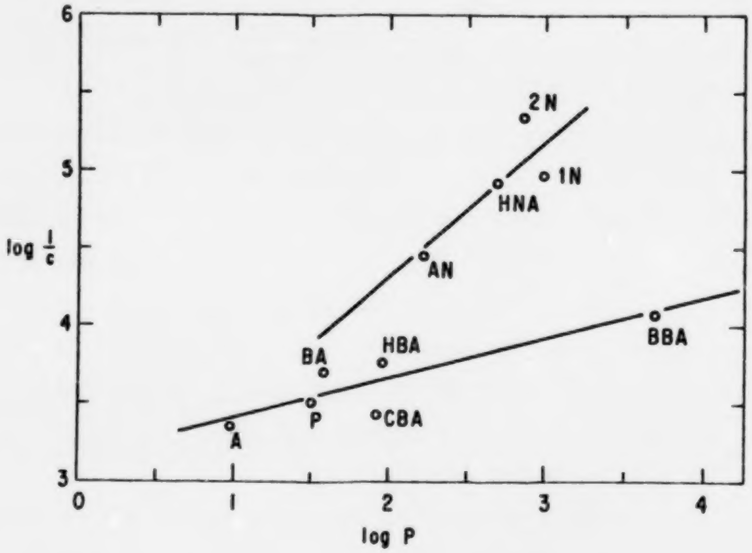


Figure 1. Acute toxicity of benzene and naphthalene derivatives as a function of partition coefficient. c = 96hLCO, mole/l; P = octanol-water partition coefficient; A=aniline; P=phenol; BA=benzoic acid; HBA=o-hydroxybenzoic acid; CBA=o-chlorobenzoic acid; BBA=p-*tert*-butylbenzoic acid; AN=1-aminonaphthalene; HNA=1-hydroxy-2-naphthoic acid; 1N,2N=1-, and 2-naphthol, respectively.

The toxicity is expressed in terms of 96hLC0 and is determined in static tests with juvenile Atlantic salmon *(Salmo salar)* at 9°C in soft tap-water. The general type of structure-activity relationships and their applications to fish toxicology were reviewed (ref. 24).

In most cases the only structural parameter used was the octanol-water partition coefficient (P). This parameter may predict the toxicity quite accurately in series of related compounds with identical or similar functional groups. In some cases, Hammett σ constants were also used as structural parameters.

As a starting point for the estimation of acute toxicity of aromatic compounds, the toxicities of several simple benzene and naphthalene derivatives are plotted against P in log-log coordinates (figure 1). The plots are linear and can be expressed by equations (4) and (5) for benzene and naphthalene derivatives, respectively.

$$\log (1/c) = 0.259 \log P + 3.13 \qquad (4)$$

$$\log (1/c) = 0.889 \log P + 2.54 \qquad (5)$$

Monosubstituted 1,2-dihydroxybenzenes. A number of these compounds with different substituents in the 4- position were patented. The acute toxicity of catechol was determined in our laboratory. The toxicity of the other compounds was estimated from equation (6), which was derived originally for nitrophenols (ref. 24) and adjusted to fit catechol, and from equation (7), which is the equation of a line parallel to that given by equation (4), but adjusted to the toxicity of catechol.

$$\log (1/c) = 1.2 \log P + 2.9\sigma + 3.48 \qquad (6)$$

$$\log (1/c) = 0.259 \log P + 4.31 \qquad (7)$$

The toxicities calculated from equation (6) were almost always higher than those obtained from equation (7); they are given in table 1. Geometrical means of these two estimates, also presented in table 1, are probably closer to reality.

Disubstituted 1,2-dihydroxybenzenes. The toxicity of these compounds was estimated as above and the results are given in table 2. It should be noted that the presence of sulfo- groups significantly decreases the acute toxicity.

Substituted benzoic acids. The toxicity estimates are based on

Table 1. Prediction of acute toxicity of 4-substituted 1,2-dihydroxybenzenes to juvenile Atlantic salmon

Substituent in position 4				96hLCO, mg/l		
	Mol. wt.	log P	σ	eq.(6)	eq.(7)	geom. mean
$HOOC(CH_2)_2$-	182	0.59	-0.05	16.6	6.3	10.2
OCH-	138	0.23	0.38	1.9	5.9	3.4
H-	110	0.88				3.2*
CH_3-	124	1.44	-0.12	1.7	2.6	2.1
$H_2C=CH_2CH_2$-	150	1.98	-0.10	0.4	2.3	1.0
HOOCCH=CH-	180	0.88	0.52	0.2	5.2	0.9
O_2N-	155	0.60	0.75	0.1	5.4	0.6
Cl-	145	1.59	0.30	0.1	2.8	0.5

*Determined value.

equation (4) and the results are summarized in table 3. In general, the introduction of a carboxyl decreases the toxicity of these compounds.

Various benzene derivatives. The toxicity of 1,3-dihydroxy-2,4-dinitrobenzene was calculated from the equation used for nitrophenols (ref. 24); the toxicities of the remaining two compounds were obtained from equation (4). The results are presented in table 4.

Substituted naphthalenes. The toxicity of substituted naphthalenes was estimated from equation (5). It is interesting to compare the toxicity of 1-hydroxy-2,4-dinitronaphthalene with that of 2,4-dinitrophenol. If the prediction for the former compound is correct, then its higher toxicity is caused entirely by the increased partition coefficient. As in the case of benzenesulfonic acids, the toxicity of naphthalenesulfonic acids is expected to be relatively low (table 5).

Aliphatic compounds. Compounds of this class, found in the patent literature, are listed in table 6. Related reference compounds are not available and the toxicities could not be estimated. It is likely that these compounds are not very toxic.

Table 2. Prediction of acute toxicity of disubstituted 1,2-dihydroxybenzenes to juvenile Atlantic salmon

Substituents	Mol. wt.	log P	σ	96hLCO, mg/l eq.(6)	 eq.(7)	 geom. mean
4,6-disulfo-	270	-8.64	0.14	8×10^{11}	2300	*
4-methyl-5-chloro-	158	2.15	0.18	0.04	2.1	0.29
3-methyl-5-*tert*-butyl-	180	3.42	-0.27	0.03	1.1	0.18
3,5-di-*iso*-propyl-	194	3.94	-0.22	0.01	0.9	0.06

*Practically nontoxic.

Table 3. Prediction of acute toxicity of substituted benzoic acids to juvenile Atlantic salmon

Substituents	mol. wt.	log P	96hLCO, mg/l eq.(4)
Benzoic acid	122	1.71	24*
- 2,4,5-tricarboxy-	255	-0.55	260
- 2,4-dihydroxy-	154	0.37	92
-3-carboxy-4-hydroxy-	182	0.72	89
-2,4-dicarboxy-	210	1.07	81
-4-ethoxy-2-hydroxy-	182	1.42	57

*Determined value.

Table 4. Prediction of acute toxicity of various benzene derivatives to juvenile Atlantic salmon

Compound	Mol. wt.	log P	σ	96hLC0, mg/l, eq.(4)
1,3-dihydroxy-2,4-dinitrobenzene	176	0.14	1.14	0.7[a]
4-hydroxyacetophenone	136	1.10	--	>30[b]
2,4-dihydroxyacetophenone	152	0.15	--	100
2-hydroxy-5-methyl acetophenone	150	1.57	--	43

[a] Log (1/c) = 1.2 log P + 2.91σ (ref. 24).

[b] Determined value.

Table 5. Prediction of acute toxicity of substituted naphthalenes to juvenile Atlantic salmon

Compound	Mol. wt.	log P	96hLC0, mg/l, eq. (4)
1-hydroxy-2,4-dinitro-	234	2.42	4.8*
2-carboxy-3,5-dihydroxy-	204	1.99	3.4
1-amino-2-hydroxy-4-sulfo-	239	-3.15	100

*0.06 from eq. log(1/c) = 1.2 log P + 2.91σ, σ = 1.27; compare to 0.25 for 2,4-dinitrophenol (ref. 24).

Table 6. Alicyclic and aliphatic compounds of low toxicity

1,2,3,4-cyclopentane tetracarboxylic acid
1,2,3,5-tetrahydroxycyclohexane carboxylic acid
hexahydroxycyclohexane
1,3-dihydroxy-2-propanone
1,3-dihydroxy-2-butanone
1,4-dihydroxy-2-butanone

Table 7. Acute toxicity of amines to juvenile Atlantic salmon

Compound	Mol. wt.	96hLCO, mg/l
Polyalkylene imines		
$H_2N\text{-}(CH_2CH_2NH)_x\text{-}CH_2CH_2\text{-}NH_2$ x = 0-3	103-189	20-30
Long chain aliphatic amines		
Dodecyl amine $C_{12}H_{27}N$	185	1-5
Hexadecyl amine $C_{16}H_{35}N$	241	--
N-alkyl diamines		
$RNH\text{-}(CH_2)_x\text{-}NH_2$, $R = C_8\text{-}C_{22}$, x = 2-4	--	--
N-coco-propylene diamine	270	<1

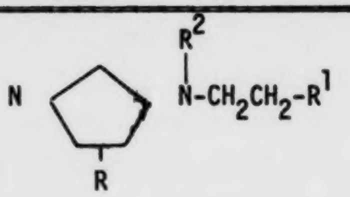
Amines and imidazolines. No structure-activity relationships are as yet available for these compounds. The data obtained experimentally in our laboratory are summarized in tables 7 and 8, and indicate a relatively high toxicity. Sulfuric acid was used to control pH in tests with polyalkylene imines. In the case of the substituted imidazolines, quaternarization by benzyl and 2-(sodium carboxy)-ethyl does not have much effect on the acute toxicity, except for the amphoteric "coco" derivative, which is nontoxic at 10 mg/l. Similarly to other surfactants, the length of R may strongly affect the toxicity.

Surfactants. A variety of surfactants may be used in well drilling operations. Some of the typical products are listed in table 9. Partition coefficient-based structure-activity relationships are not available for this class of compounds. The toxicity may be correlated with the length of the aliphatic chain of alkylbenzene sulfonates, and reaches a maximum at about C_{16}-C_{18}. The toxicity of nonionic surfactants is related among other things to the length of the oxyethylene chain and decreases with increasing length of the chain. Extensive literature is available on the toxicity of surfactants to aquatic fauna (see for example ref. 25). The acute toxicity ranges from less than 1 to more than 100 mg/l, but, the acute toxicity data can be particularly misleading. A delayed mortality may occur after exposure to concentrations as low as 1/3,000 of 24hLC50 (ref. 26), and chemoreceptors of aquatic fauna may be possible targets in sublethal exposures (ref. 27). Some surfactants may also simulate biological activity of natural compounds such as steroid glycosides of starfish (ref. 28). Alkyl polyglycol ethers are taken up by fish (ref. 29), and residues of anionic surfactants in the mg/kg range were detected in some fish and shellfish (ref. 30).

Quaternary ammonium salts with C_{16}-C_{18} alkyls are very toxic, but their toxicity may be at least partly moderated by adsorption on suspended solids (ref. 31). Dimethyl-dicoco-ammonium chloride, patented for use in drilling operations, has a 96hLC0 of 0.9 mg/l.

The acute toxicity (96hLC0) of petroleum sulfonates was 3.7, 1.9, and 3.1 mg/l for preparations with an average molecular weight of 350,

Table 8. Acute toxicity of substituted imidazolines to juvenile Atlantic salmon



R	R^1	R^2	Mol. wt.	96hLCO, mg/l
C_{12} - C_{20}	NH_2 or OH	--	--	--
Coco($C_{13}H_{27}$)	OH	--	296	2.5
Stearyl($C_{17}H_{35}$)	OH	--	352	0.6
Coco	OH	$C_6H_5CH_2$	404	1.0
Stearyl	OH	"	460	3.5
Dodecyl($C_{11}H_{23}$)	OH	CH_2CO_2Na	366	>35
Coco	OH	"	394	>10
Stearyl	OH	"	450	4

Table 9. Typical surfactants used in drilling muds

Ethylene oxide adducts of:	Sulfated or sulfonated:
Castor Oil	Castor Oil
Phenol	C_{15}-C_{18} aliphatic hydrocarbons
Nonyl phenol	Dodecyl benzene
	Petroleum

450, and 500, respectively. Petroleum sulfonates are quite ill-defined products and their toxicity may be very much affected by the composition of the parent petroleum stock.

Bactericides. These compounds are generally highly toxic to aquatic fauna. Preference should be given to compounds with higher solubility in water and lower P. The use of pentachlorophenol should be eliminated because of its high toxicity, bioaccumulation potential, and the presence of toxic impurities such as chlorinated dibenzodioxins, dibenzofurans, and diphenyl ethers.

CONCLUSIONS

The presented data indicate that under normal circumstances the most pronounced detrimental effects on the environment may be caused by the physical action of suspended solids from the drilling muds. The high molecular weight organic constituents of drilling muds are relatively nontoxic, the molecular weight constituents have toxicities ranging from high to relatively low, and it may be possible to select technically satisfactory compounds that are not very toxic. The same may be true about surfactants.

Little is known about the effects, encountered during the drilling, of high temperatures on the organic additives. Hydrolysis of polymers and elimination of some functional groups may take place. The products of these reactions could have higher toxicity than the parent compounds.

Some drilling muds may contain certain petroleum fractions or tar. An extensive literature on the effects of these materials on the aquatic environment is available and it is obvious that the discharge of these substances should be limited as much as possible.

An attempt was made to estimate the acute toxicity of a number of compounds by structure-activity relationships. Time will tell how successful this approach is. It would certainly be useful for a better and systematized understanding of environmental properties of chemicals.

ACKNOWLEDGMENT

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DISCUSSION

MR. JACK W. ANDERSON (Texas A&M University, College Station, Texas): Dr. Zitko, I think the method of evaluation of the different toxicants was very interesting. I think the problem was in the evaluation of the effects of sediments. You got your data or your data is produced from, what, the northwest or northeast? I think there is a little bit of difference between those waters and the estuarine and near-shore waters of the Gulf of Mexico, where our sediment loads are much greater. And I think that you were talking in low milligrams per liter, I believe. I think that would be unusual. Of course, it is expected that the drilling operations will be extended in the clearer waters, but I think for a lot of the waters of the Gulf of Mexico the organisms are accustomed to rather high turbidities and high sediment loads.

DR. ZITKO: Yes. I agree completely with you. It depends, really, on the area. And I am sure the conditions are different in the Gulf of Mexico.

MR. WAYNE H. McKENZIE (Milchem, Inc., Houston, Texas): So far we have heard the word toxicity, but from the various papers we have heard how toxicity is measured as 96-hour LC_{50}, 96-hour TL_{50}, 96-hour LD_{50}, 96-hour LT_{50}. I wonder if you might go into some of these differences in terminology for comparison purposes; exactly what they mean?

DR. ZITKO: Ninety-six-hour LC_{50} and 96-hour TL_{50} are synonymous and refer to a concentration (mg/l) that kills 50 percent of the test animals in 96-hours. LD_{50} is a dose in mg/kg body weight that kills 50 percent of the test animals. LT_{50} is time to 50 percent mortality. I think somebody yesterday had a graph of LT_{50} plotted against concentration. Reading from the curve at 96 hours he determines the 96-hour LC_{50}. This approach is fine as long as you have mortalities within that time.

In our experience, what usually happens is that there is a breakoff point in the curve before you reach 96 hours.

We talk in terms of the 96-hour lethal threshold (LCO), which is the geometric mean of the highest concentration where we do not get mortality and the lowest concentration, where we still get an LT_{50} value. On the other hand you have to keep in mind that the variety of aquatic fauna is tremendous, and the sensitivity of different species varies appreciably, not only between the species, but even the same species may have different sensitivities depending on the season. One has to be very careful in talking in terms of acute toxicity. It more or less ranks the compounds, but really it is very difficult to translate acute toxicity data into environmental effects.

MR. PAT M. WENNEKENS (Alaska Department of Fish & Game, Anchorage, Alaska): I have two questions. One is that the information you have gathered pertains to freshwater systems, from what you showed. Once those things are being introduced into the marine environment, they get into a complex ionic solution. My first question is, what kind of prediction do you have in terms of changing the chemical composition or phase that would provide differences in toxicity, as you are getting into pretty complex ion solutions?

My second question relates to your test program. Did you make those measurements on the early embryonics and juvenile stages of some of the forums rather than the adults, at which stage they are much more sensitive to different types of compounds?

DR. ZITKO: To the first question, the answer is complex. It depends on the type of compound. Some compounds may be more toxic in seawater than they are in freshwater, and for some compounds it would be the other way around. It depends on the character of the compound. So ionic compounds may be less toxic in seawater than they are in freshwater; on the other hand, highly lipoplinlic compounds may be more toxic in seawater than they are in the freshwater. An example of this is an exotic compound, the yellow phosphorus. Yellow phosphorus is more toxic in seawater than in freshwater. And it depends on the basic physiology of the fish, because in the seawater they really have to drink water and in freshwater it is the other way around. So it is a complex situation.

I would say that ionic compounds, such as phenols, may be less toxic in seawater than they are in freshwater.

We are doing our tests mostly on juvenile Atlantic salmon, but I agree with you that once you have several life stages of a certain animal, the embryonic forms are not necessarily the most sensitive ones. It depends. There is no general rule what to do.

MR. DENNIS G. WRIGHT (Environment Canada, Winnipeg, Manitoba, Canada): Dr. Zitko, I would like to thank you for the plug for the two Environment Canada papers, those being the Falk and Lawrence report, and also the Bernard Land literature review. These papers are available from our Winnepeg office, Environment Canada. And if you would like, I can get copies for any of you who are interested, if you would just care to give me your name and address I can have them sent out.

I would also like to say that Environment Canada and the Arctic Petroleum Operators Association have been engaged in a 2-year study program, as Bob Weir mentioned yesterday, looking at the environmental effects of drilling fluids. And we are going to be producing three rather large volumes of papers sometime this summer as a result of these studies; hopefully these will be available to the U.S. people as well.

Again, if you would like these papers, as well, could you leave your name and address with either Bob Weir or myself.

22 May 1975

Session II: (con.)

ENVIRONMENTAL IMPACT OF CHEMICALS USED IN WELL DRILLING

C. S. Giam, Ph.D.
Chairman

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POTENTIAL EFFECTS OF OIL DRILLING AND DUMPING ACTIVITIES ON MARINE BIOTA

Robert Y. George, Ph.D.*

Abstract

The objective of this paper is to provide a base for discussing the possible perturbations of oil drilling activities on the biota inhabiting the inner and outer continental shelf regimes. A perusal of literature on this subject points out clearly our inadequate knowledge on the impact of drilling mud components on marine biota and our meager understanding of the chronic effects of spillage of oil on both plants and animals in the marine environment.

On the basis of results obtained in recent offshore ecological investigations in the Louisiana Continental Shelf, efforts are made to evaluate the extent of effects of drilling activities on the biota and the physical environment adjacent to oil platforms. In recognition of the need for arriving at models depicting the impact of drilling activity on the marine ecosystem, inferences are drawn here to consider biological implications of potential effects of drilling discharges under the following four aspects:

(1) Impact of drilling materials causing "burial effect" on the seafloor benthos.

(2) Discharge of drilling mud components and their possible accumulation or magnification in the food chain.

(3) Influence of turbidity-plumes of drilling mud on the filter-feeding fouling organisms.

(4) Acute and chronic effects of spillage of crude oil on marine biota.

INTRODUCTION

The fundamental question posed in this paper can be simply asked as follows: What are the acute and chronic effects of the addition of various

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inert and toxic substances used in the oil drilling process on the marine biota? It is realized that the compounds of oil-base or brine-water-base drilling mud enter the marine environment as adherent particles of the drill cuttings that are generally dumped in the site of drilling. This drilling operation evidently promotes a localized alteration in the environment, both in the water column by way of resuspension and redistribution of particulate matter, and in the benthic regime by the deposition over the bottom sediments of material containing cuttings and drilling mud. It is known that in the Louisiana inner and outer continental shelf environment drilling mud was introduced into the ecosystem during the process of drilling oil wells since the inception of the first well in 1947. The typical ingredients of the drilling mud include materials such as barium sulphate, bentonite clay, hydrated lime, caustic-sodium hydroxide as well as the most common additive, Ferrochrome Lignosulfonate, which is a waste byproduct of the paper industry (ref. 1). Different compounds are used to obtain various properties such as weight (barite), viscosity (density materials), suspension (clay), bacteriocide (paraformaldehyde), and lubricating agents (diesel oil). The precise effect of these different components of the drilling mud on the survival and physiological performance of marine animals has not been critically examined thus far in any long-term experiments in the laboratory or in the natural environment. However, experimental studies have been performed to test the toxicity of the composite drilling mud for establishing 50 percent lethal dose levels (LD 50 or also known as tolerance limits - TL50) with a standard exposure period of 96 hours. These acute studies give clues as to the critical concentration levels, generally exceeding 1,000 ppm, that induce deleterious effects in the marine biota. In most cases such high levels reach near-saturation limits and in fact, the dynamic process of dilution caused by water movement in the marine environment leads to drastic reduction of these concentrations. The effect of certain components of the water-base drilling mud on marine biota was first investigated by Daugherty in the early fifties in Louisiana coastal environment (ref. 2). He essentially reported on the nontoxic nature of such components as bentonite and barite on marine life. Nevertheless, to date we do not possess data on the sublethal or chronic effects of such drilling mud components which are usually used in small quantities and can cause concern if accumulation takes place in marine biota.

Field observations provide information concerning the quantities of drilling fluid and drill cuttings discharged during drilling operations. The drill cuttings appear to contain primarily sand and shales, which tend to descend to settle on the bottom rather rapidly due to gravity. Drill cuttings are not commonly encountered at the base of the producing platforms in the Louisiana shelf, and the shales offer a new substratum for the settlement of larvae of sessile fouling organisms such as the acorn barnacles. On the contrary, the drilling mud when discharged does not sink rapidly but produces a plume of turbidity in the upper layer of the water through the water column down to the bottom. The concentration of this plume depends on the density stratification of the water column. Its prolonged existence can cause effects of biological consequence on the plankton in the surface, the nekton in the midwater, and the benthos on the sea floor. The influence on the biota can be considered as acute effects in short-term conditions. Furthermore, the effect on biota should be treated with reference both to physical interference of biological processes, such as photosynthesis and respiration due to the turbidity-producing mud compounds, and to the chemical aspects of toxicity-causing mud compounds. Generally, the mud additives of clay-type emulsions have a relatively low level of toxicity. As pointed out earlier, laboratory experimental data are lacking on chronic effects of drilling mud compounds on the marine animals. In the marine environment, the effect is apparently localized since the drill cuttings are generally found to occur within 100 feet from the nucleus of the oil platforms in Louisiana shelf. However, the suspended drilling mud can get carried by currents to distant locations from the point of origin. In the drilling operation, effort is made to recover the drilling mud for reuse and the major portion of mud components enter the marine environment as adherent particles of the drill cuttings that are generally dumped into the sea.

In my opinion, the concern on effects of the inert mud components on the marine ecosystem should be examined in the perspective that mud is not an alien material to the ocean. It turns out that over 70 percent of the ocean floor is made up of a mud-type substratum that is known to support a variety of marine life. The floor of the abyssal plain has a continuous bed of red clay sediment with occurrence of manganese nodules. The continental slope and rise include vast stretches of brown or green mud with a mixture of globigerina ooze. Mud flats along the shore are not uncommon. In the continental shelf environment with mud bottom conditions such as in the areas off Louisiana, the presence of mud-laden layers dominate the near bottom depths in the water column. It is estimated that the daily dumping of mud by the Mississippi River into this shelf region exceeds over a million tons. The influence of the Mississippi mud or the drilling mud is primarily a physical phenomenon due to the production of turbidity plumes. The point for consideration is the potential effect of seepage into biological systems of small quantities of substances which can cause disruptions.

Although our knowledge on the impact of the drilling mud additives on marine biota is meager today, it is important to focus on potential effects and delineate specific investigations in conjunction with the current OCS oil and gas development. I have chosen to deal with potential effects under four distinct categories as follows:

(1) "Burial Effect" of Drilling Mud On Sea-Floor Benthos,
(2) Entry and Transport of Drilling Mud Components In Marine Food Chain,
(3) Influence of Turbidity Plumes of Drilling Mud on Organisms, and
(4) Acute and Chronic Effects of Oil On Marine Biota.

"BURIAL EFFECTS" OF DRILLING MUD ON SEA-FLOOR BENTHOS"

In the offshore environment, the rate of deposition of sediment is gradually reduced as the distance increases from the shore. In the neretic zone, mostly within 20 miles from the coastline, the sea floor is subject to active sedimentation. In general, the sediment input from land runoff is significantly higher in the sea floor environment adjacent to rivermouths and inlets. Such a benthic regime is usually characterized by a soft-bottom substratum that is largely inhabited by burrowing infaunal organisms. These animals tend to occupy the upper portion of the sediment-water interface and readjust their relative positions during the active process of sedimentation. In the offshore oceanic zone, beyond 50 miles from the shore line, sediment deposition on the sea floor is declined to very low levels. The sea floor in such offshore environment receives primarily biogenic sediments of planktonic origin. Coral reef communities prevail in deepwater zones of reduced sedimentation. In other words, the mud bottom communities are not vulnerable to active sedimentation and deposition of mud, but communities on hard substrata are evidently disturbed in the event of active mud deposition. The accumulation of drilling mud and drill cuttings on a given substratum is referred to here as the "burial effect."

During the offshore ecology investigations in the Louisiana continental shelf (1973-74) a photo-survey was made on the sea floor in the vicinity of several oil platforms to examine drill cuttings and their impact on the environment. This study was performed as part of an investigation of the types of sessile and motile organisms that flourish on the hard substratum of the platform legs. Generally drill cuttings were not found at the base of platform legs or in the adjacent regions. Most of these platforms have been in production for more than 10 years. Perhaps the deposited drill mud and cuttings were completely covered by the process of active sedimentation from the vast inflow of Mississippi River Plume. Observations on infrared and color satellite photographs show the extended plume boundaries reaching far beyond 30 or 40 miles from the shoreline. In figure 1, the undulating plume boundary and plume directions are illustrated to show the vast impact of the Mississippi River mud on the sea floor environment and biotope surrounding the numerous oil producing platforms and drilling rigs in this region of intense activity.

It is estimated that approximately 250 tons of drilling mud and about 920 tons of drill cuttings are deposited near a typical 10,000 foot Gulf Coast well (ref. 1). In recent years, a vast quantity (90 percent) of the drilling mud is recovered for reuse and only drill cuttings are dumped to the sea floor. It has been pointed out in earlier studies that drill cuttings accumulate as 20-foot piles beneath oil platforms in the California Shelf and the cuttings are found within 100 feet from the platform structures. This observation (ref. 3) suggests that the "burial effect" of drill cuttings is an extremely localized phenomenon and the impact on marine

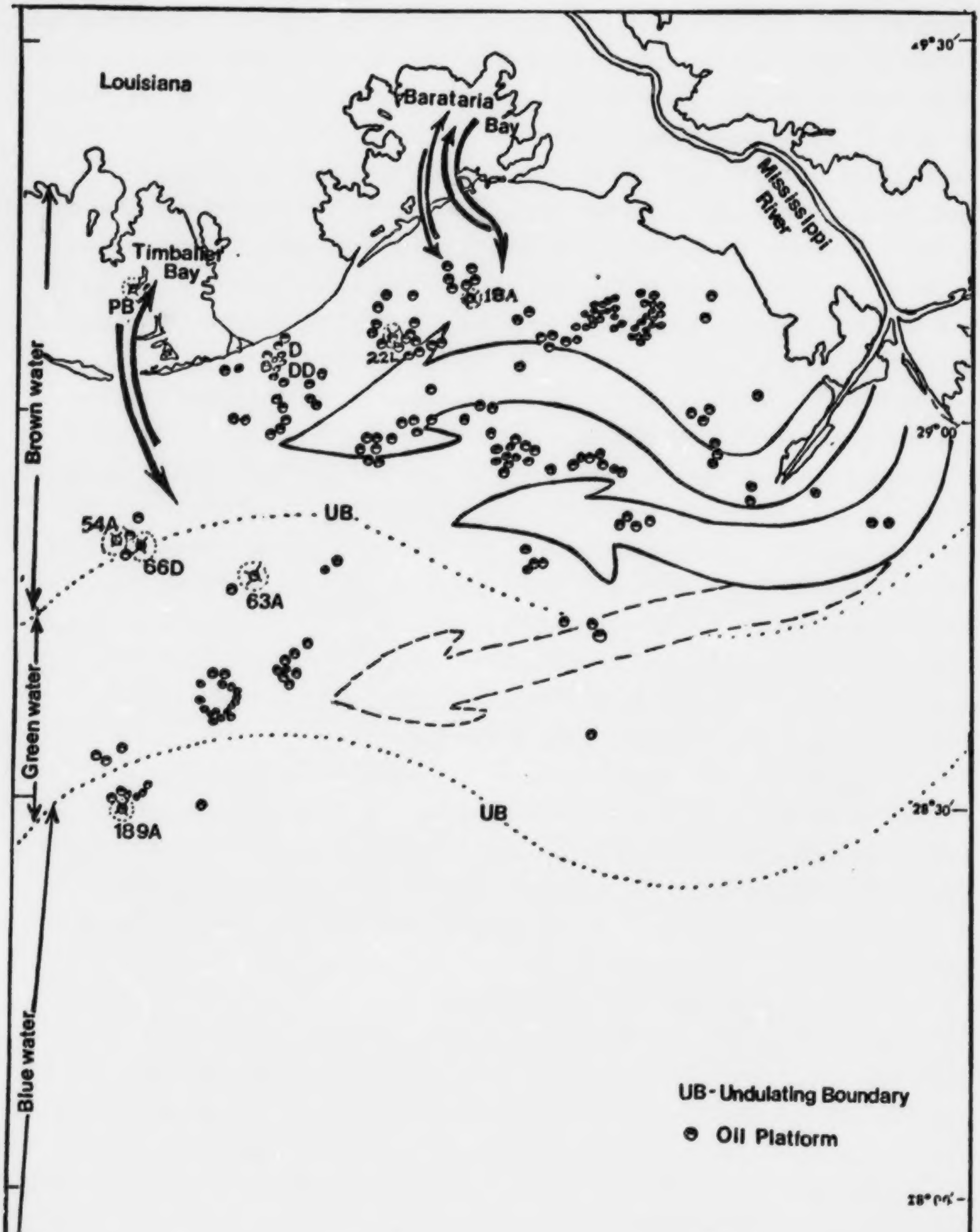

Louisiana
Barataria Bay
Mississippi River
Timbalier Bay
PB
18A
22L
D
DD
54A
66D
63A
189A
UB
UB
Brown water
Green water
Blue water
29°30′
29°00′
28°30′
28°00′
90°30′
90°00′
89°30′
UB - Undulating Boundary
● Oil Platform

Figure 1. Map of the study area showing the location of oil platforms in the Louisiana Shelf region with emphasis on the direction and magnitude of Mississippi River plume.

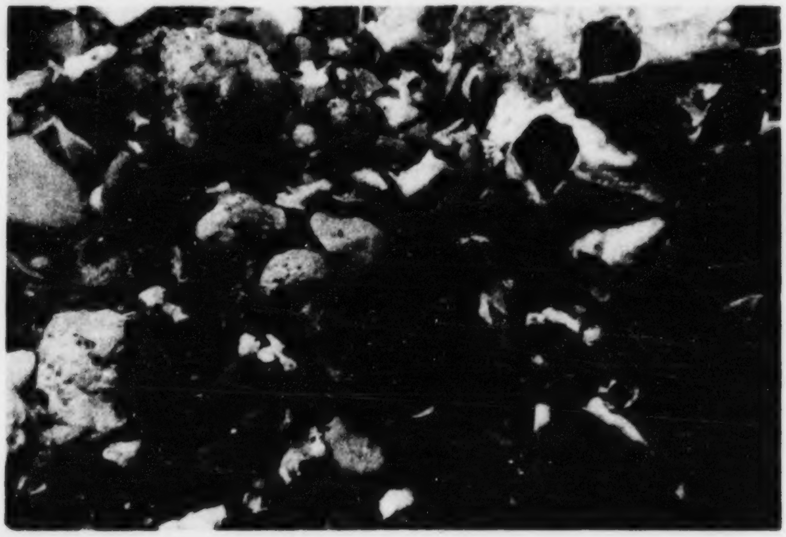


Figure 2. Underwater photograph showing the presence of drill cuttings at a depth of 54 ft in the vicinity of the Exxon Oil Platform 22L, located about 10 miles from shore in the Louisiana inner shelf (south of Grand Isle). Note the pile of drill cuttings and shales with settlement of the barnacles. (Photo taken by P.J. Thomas during the Offshore Ecology Investigations.)

communities is insignificant. Furthermore, the underwater photographs of drill cuttings seen in our studies of offshore ecology investigations in the Louisiana shelf reveal the presence of acorn barnacles Balanus eburneus (figure 2). The fouling organisms settle on drill cuttings, and perhaps the introduction of a hard substratum over the soft mud or sand bottom environment induces a "reef effect" to promote proliferation of sessile organisms and associated motile consumers.

ENTRY AND TRANSPORT OF DRILLING MUD COMPONENTS IN MARINE FOOD CHAIN

The major concern about dumping drilling mud into the marine environment is the possible injection of small quantities of some toxic mud additives into the food chain. The composition of typical drilling mud is given in table 1. Barium sulfate constitutes the major ingredient of the

Table 1. Primary components of drilling mud in order of quantitative composition--data based on Shinn's typical example (ref. 1) with a total of 506,300 lb (253 tons) used in drilling a 10,000-foot oil well

Quantity	Mud material	Order of abundance
A. More than 300,000 lb	Barium sulfate	#1
B. More than 70,000 lb	Bentonite clay	#2
C. More than 20,000 lb	Ferrochrome Lignosulfonate	#3
	Sodium hydroxide	#4
	Hydrated lime	#5
D. More than 6,000 lb	Organic polymer (Baroid Dextrid)	#6
	Lignitic material (Baroid Carbonox)	#7
E. More than 2,000 lb	Pregelatinized starch (Baroid Impermex)	#8
F. Less than 400 lb	Defoamer (Aluminum Strearate)	#9
	Defoamer (Baroid Surflo W300)	#10

drilling mud, representing more than 90 percent of the weighting agents. Barite used in drilling fluid contains such compounds as silica and iron oxide. Benthonite clay is essentially an inert component. In addition to the compounds given in table 1, certain other chemicals are used in the well-completion process; these include calcium chloride and lignin. In the oil-based mud, preferably used in drilling deep wells, the lubricating oil serves as a potential hydrocarbon carrier.

The focus here is an empirical elucidation of potential routes of transfer of small quantities of possible toxic substances in a typical marine food chain. These compounds can occur in the ambient medium, both in water and sediment, in the form of particulate or dissolved compounds. These elements or compounds may find their routes through the food chain directly into the various trophic levels by means of ingestion by the organisms, or they can pass from one trophic level to a higher level in the food chain as illustrated in a diagramatic fashion in figure 3. We do not possess data to show whether any accumulation of a specific compound of drilling mud can occur in any plant or animal in the food chain. We do not possess any data to show magnification of the substances in higher trophic spectra. Most of the compounds, including barium, are naturally found in minute quantities (ppb) in biota, particularly in skeletons. Silica is encountered as a building material of the exoskeleton in marine organisms, including silicoeous diatoms. Calcium carbonate constitutes a major compound in shell-bearing mollusks and corals. In the blood pigment hemoglobin iron becomes an integral part. These elements occur in trace quantities in the marine organisms. Furthermore, marine animals show selective absorption of elements and compounds by appropriate physiological mechanisms of ionic regulation. An organism maintains an equilibrium with the bioavailable elements of its environment. In conditions of stress due to increased levels of these elements, the organisms accumulate the compounds in specific organs and also eliminate the same as metabolites or excreta to the external environment.

As illustrated in figure 3, the potential impact should be considered under three distinct categories. First, it should be borne in mind that in a given community, different populations and even different individuals within a population can respond differently to the presence of certain levels of a substance. As a result of various responses by the different species in a community, consequent alteration in the community structure and function can come about in response to the effects of the introduction of new compounds. The loss of certain susceptible species and the survival of resistant species induces a change in the population dynamics and food chain in the biotic community.

The second type of potential impact is not necessarily related to mortality or survival. In conditions of altered chemical environment, certain processes related to growth, reproduction, or larval development can exhibit either retardation or acceleration.

Thirdly, the potential impact is such that the organisms in the community either do not exhibit any modification or else they adjust effectively through physiological processes. This condition does not represent any disruptive change and therefore is regarded as a "negative impact." The

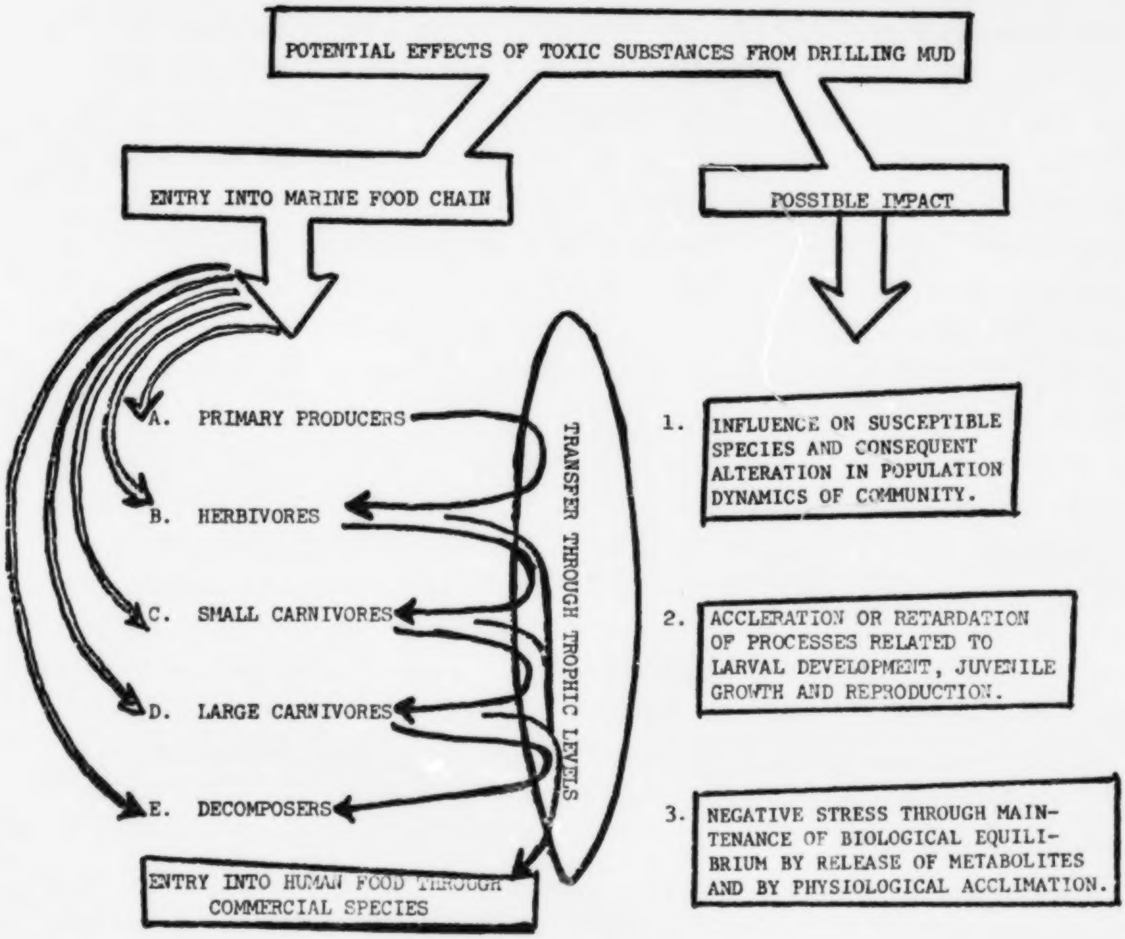

POTENTIAL EFFECTS OF TOXIC SUBSTANCES FROM DRILLING MUD
ENTRY INTO MARINE FOOD CHAIN
POSSIBLE IMPACT
A. PRIMARY PRODUCERS
B. HERBIVORES
C. SMALL CARNIVORES
D. LARGE CARNIVORES
E. DECOMPOSERS
TRANSFER THROUGH TROPHIC LEVELS
ENTRY INTO HUMAN FOOD THROUGH COMMERCIAL SPECIES
1. INFLUENCE ON SUSCEPTIBLE SPECIES AND CONSEQUENT ALTERATION IN POPULATION DYNAMICS OF COMMUNITY.
2. ACCLERATION OR RETARDATION OF PROCESSES RELATED TO LARVAL DEVELOPMENT, JUVENILE GROWTH AND REPRODUCTION.
3. NEGATIVE STRESS THROUGH MAINTENANCE OF BIOLOGICAL EQUILIBRIUM BY RELEASE OF METABOLITES AND BY PHYSIOLOGICAL ACCLIMATION.

Figure 3. Diagramatic representation of environmental impact of drilling mud additives.

addition of inert materials, such as the main components of drilling mud, also possibly imposes a negative impact.

On the basis of feeding habits we can infer that mud-eating or detritophagous animals are more susceptible to the impact of drilling mud than are carnivorous animals. In the structure of a benthic community, the loss of mud-eating populations can bring about changes in species diversity and community organization. The impact of any foreign substance to a biotope causes changes not only at the community or population level but also at the individual and cellular level in promoting or retarding processes related to growth and reproduction. When stress is applied to a system in ecological and physiological equilibrium, reactions occur at the cellular level and consequently at the individual, population, community, and ecosystem level until the system recovers equilibrium. This stress and reaction phenomena are diagramatically illustrated in figure 4.

The marine environment is a receptacle for a variety of materials both as a result of natural events and as a consequence of man's activities. The approximate quantities of input of some selected heavy metals, nutrients, and synthetic organic chemicals have been tabulated, with approximate amounts of drilling mud components that possibly entered the marine environment during the establishment of about 100 oil wells (table 2). This comparison offers overwhelming evidence as to the relatively small quantity of drilling mud compounds dumped in specific locations, particularly in the drilling sites. Nonetheless, it is essential that special efforts be made to monitor this flux of chemicals into the marine habitats and the subsequent flow through the food chain.

INFLUENCE OF THE TURBIDITY PLUMES OF DRILLING MUD ON ORGANISMS

The dumping of drilling mud generates turbidity plumes in the vicinity of drilling sites. In the estuarine and coastal environment, turbid conditions are normally encountered and several animals are adapted to cope with such turbid conditions. Turbid water can interfere with vision in animals and can disturb behavioral patterns of migratory fish or shrimp populations. Murky water is often attributed to the suspended sediment. However, algae

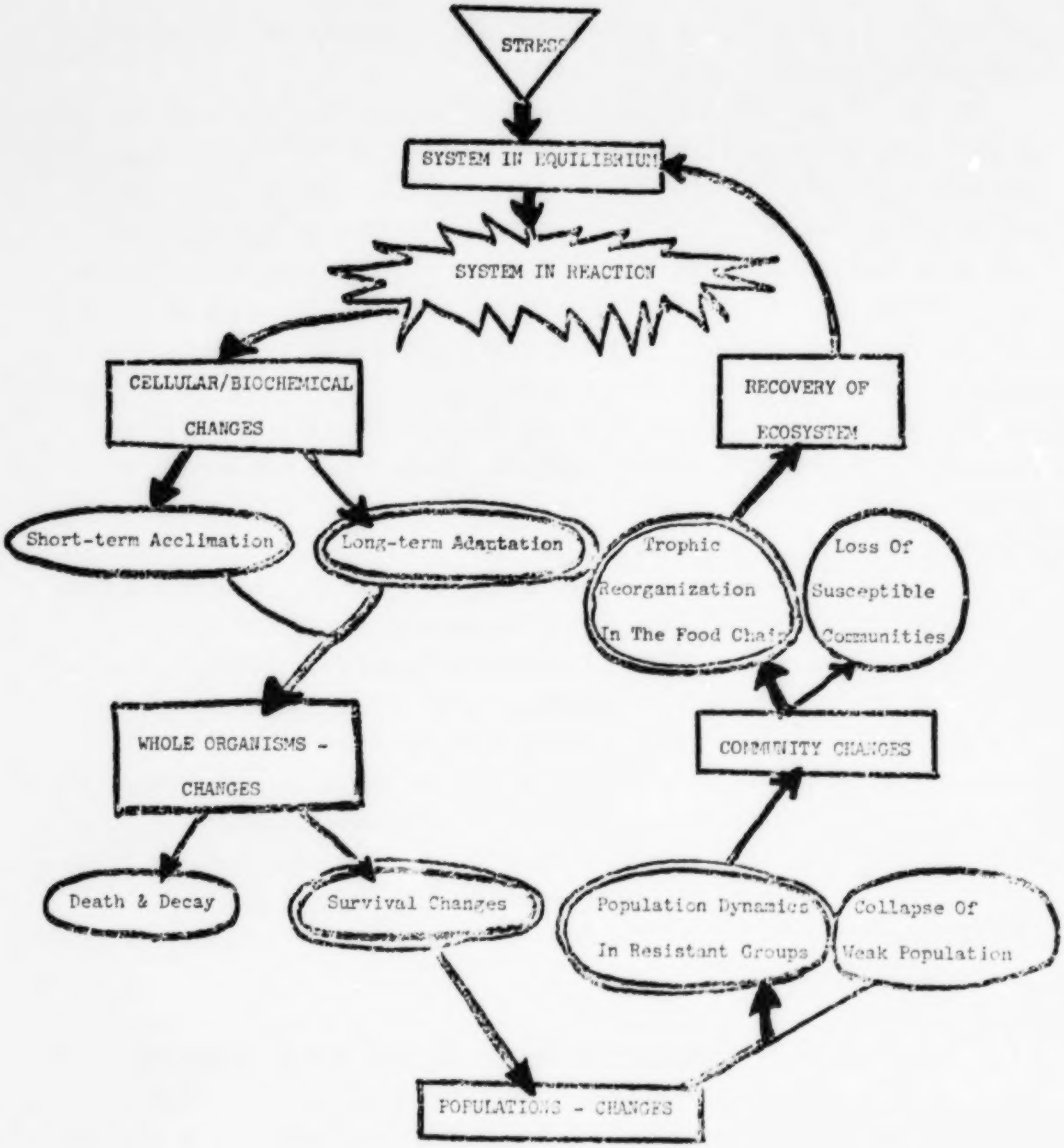

STRESS
SYSTEM IN EQUILIBRIUM
SYSTEM IN REACTION
CELLULAR/BIOCHEMICAL CHANGES
Short-term Acclimation
Long-term Adaptation
WHOLE ORGANISMS - CHANGES
Death & Decay
Survival Changes
POPULATIONS - CHANGES
Population Dynamics In Resistant Groups
Collapse Of Weak Population
COMMUNITY CHANGES
Trophic Reorganization In The Food Chain
Loss Of Susceptible Communities
RECOVERY OF ECOSYSTEM

Figure 4. Potential responses of ecosystem to stress.

Table 2. Approximate estimates of total input into the marine environment of materials or substances of potential biological concern

No.	Material	Quantity	Source
1.	Oil (petroleum hydrocarbons)[a]	2.6 million tons/yr	Ref. 4
2.	Nutrients (N) discharge through rivers	7-78.5 million tons/yr	Ref. 5
3.	Nutrients (P) discharge through rivers	2.00 million tons/yr	Ref. 6
4.	Heavy metal: lead	0.74 million tons/yr	Ref. 7
5.	Heavy metal: copper	0.25 million tons/yr	Ref. 8
6.	Heavy metal: zinc	0.70 million tons/yr	Ref. 8
7.	Synthetic organic chemical/DDT	0.25 million tons/yr	Ref. 4
8.	Polychlorinated biphenyls (PCB)	0.25 million tons/yr	Ref. 4
9.	Barium sulphate[b]	0.0013 million tons/100 oil wells	Ref. 1
10.	Bentonite clay[b]	0.0004 million tons/100 oil wells	Ref. 1
11.	Hydrated lime[b]	0.0002 million tons/100 oil wells	Ref. 1
12.	Caustic - sodium hydroxide[b]	0.0002 million tons/100 oil wells	Ref. 1
13.	Ferrochrome lignosulfonate[b]	0.0003 million tons/100 oil wells	Ref. 1

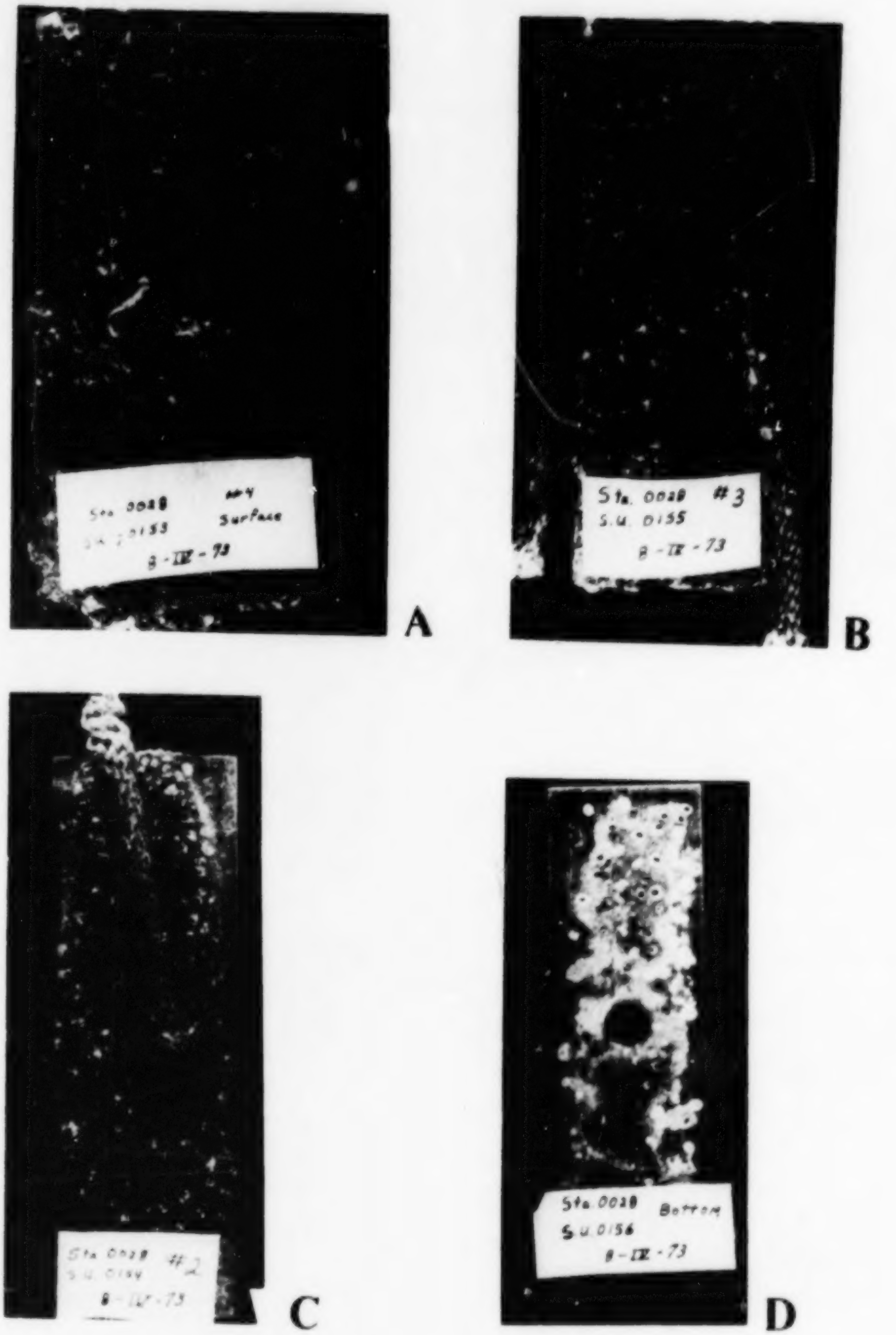
[a] Exclusive of atmospheric input.

[b] Components of drilling mud, input quantity representing rough estimate based on available figures from Louisiana Shelf.

or diatom blooms also cause turbid conditions that are comparable to sediment turbidity. Furthermore, in the near-bottom depths, settling particles accumulate to form clouds of extremely fine particles. This layer was recognized by Ewing and Thorndike as a "nepheloid" (ref. 9) layer caused by suspended matter in the deepwater. The question here is addressed to the influence of such turbid conditions on the biota. Midwater animals, which are good swimmers like fishes, squids, and motile crustaceans, can escape from turbid conditions to nearby clear-water zones. On the contrary, sessile or fixed animals such as the fouling organisms (barnacles, hydroids, bryzoans, sea anemones, and corals) cannot dislodge themselves from their substrata to avoid the ambient turbid conditions. If the occurrence of the turbid layer is an intermittent phenomenon, the sessile animals tend to reduce or cease their activities and then resume their normal activities in favorable conditions. A special effort was made to study the responses of fouling organisms on platform structures in the Louisiana shelf and Timbalier Bay with reference to the presence of a "turbid layer" (ref. 10).

The growth of fouling communities was investigated by suspending test panels in the Timbalier Bay, where drilling activity persisted during the summer of 1973. The baywaters remained murky, with peak turbidity at near-bottom depths. The fouling biomass reached peak levels as high as 3,800 g/m^2 in the surface and upper layers. Significant reduction in biomass and diversity of fouling was encountered in the turbid zone at near-bottom depths (figure 5). The occurrence of juvenile and empty barnacles in the turbid layer suggests that the growth of these cirripped crustaceans was hindered by the turbid conditions.

Turbidity variations were seen through the year with obvious seasonal peaks in the Louisiana shelf. During the post-flood period in spring and summer, 1973, a near-bottom turbid layer was detected on the Louisiana shelf. In the summer the dissolved oxygen level in the turbid zone reached unusual minimum conditions of less than 15 percent saturation level (ref. 11). Evidently, prolonged existence of such a situation can cause stressful conditions to such sessile biota as the fouling community on the platform legs. In situ underwater photographs reveal the presence of cloudy conditions caused by the accumulation of suspended particles at near-bottom depths (figure 6). The filter-feeding fouling animals are adversely


Sta. 0028 #4
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A
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8-IX-73
B
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S.U. 0154
8-IX-73
C
Sta. 0028 Bottom
S.U. 0156
8-IX-73
D

Figure 5. Photographs of submerged test panels (15cm x 5cm x 0.6cm) with fouling growth which occurred over a period of the summer 1973 (May 4 - August 4). These panels were exposed in the Timbalier Bay where drilling activity persisted in the Gulf Drilling Field. Note the occurrence of dense fouling in the surface panel and the reduction of fouling only to few barnacles in the zone of turbidity-plume at the bottom.

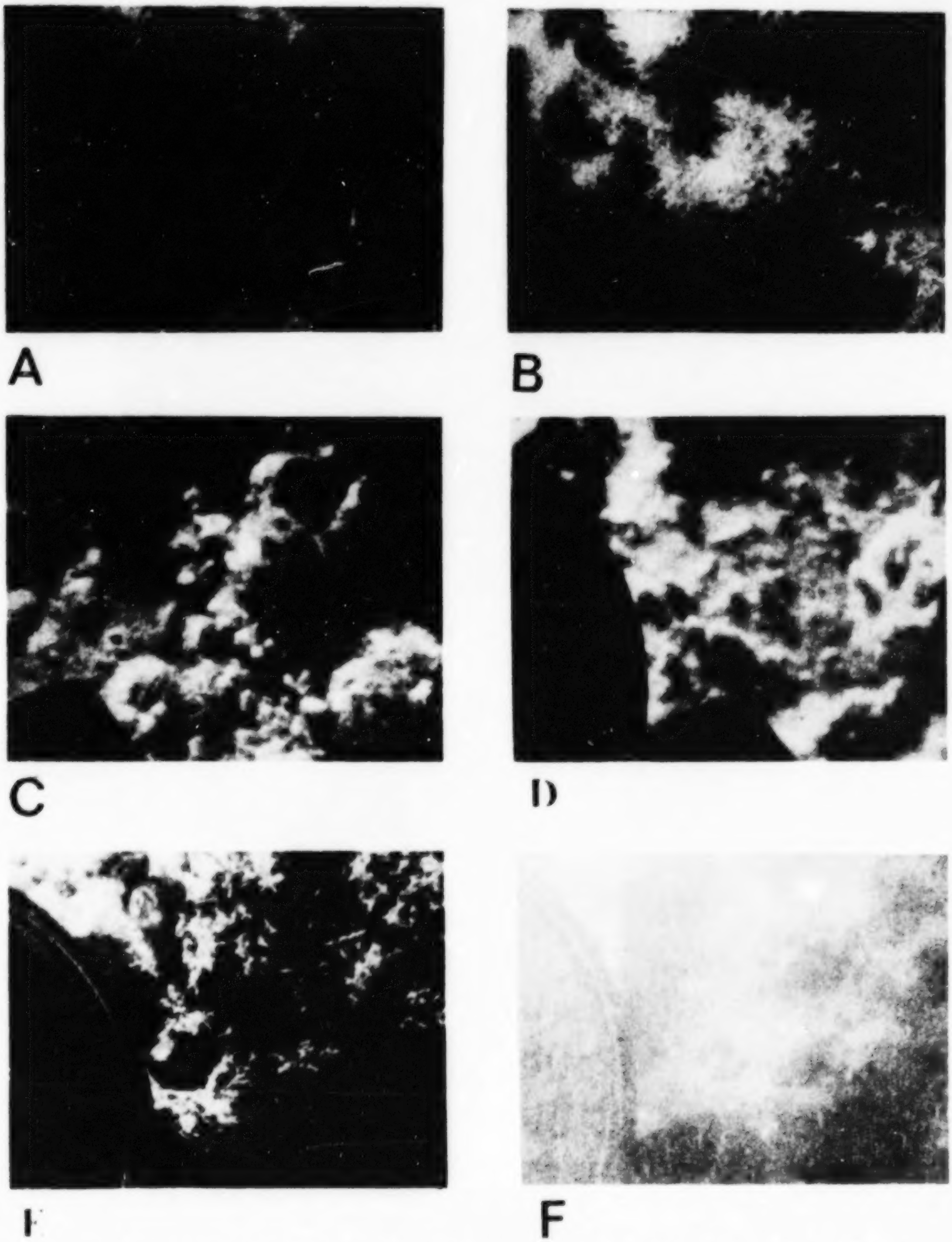

Figure 6. An assemblage of in situ photographs of fouling growth on Exxon Platform 54A from the surface (A) to increasing depths (B-E) down to the bottom (F) at 50 feet. Note the turbidity plume over prevailing fouling mat of hydroids at the near bottom depths (F). This platform is located in the Louisiana Shelf south of Timbalier Bay.

affected by the turbidity, and continuous stress can lead to mortality. Our observations suggest that the influence of turbidity plumes caused by the "nepheloid layer" or drilling mud is basically a physical phenomenon that interferes with normal feeding and reproductive activity of sessile organisms. However, this adverse effect is highly localized and this impact is an intermittent event.

ACUTE AND CHRONIC EFFECTS OF OIL ON MARINE BIOTA

In the recent years, petroleum hydrocarbons have received considerable attention with reference to their levels in water, sediment, and important marine animals in the food chain (ref. 12 and 13). Petroleum hydrocarbon enters the marine environment through industrial or municipal effluents, and by means of accidental spills during transportation or oil-well blowout, natural seepage, transport of particles through atmosphere and in relatively very small quantities through the lubricating oil of the drilling mud.

The petroleum hydrocarbon level is extremely high in oil-polluted habitats, as shown in the West Falmouth sediment samples (ref. 14). The hydrocarbon level in the Louisiana coastal waters tends to remain two or three orders of magnitude higher than in open gulf waters. The hydrocarbon levels have been reported for marine plants and animals in recent studies (table 3). The question is: What are the biological implications of hydrocarbon levels in marine environment and biota? It is realized that the acute effects have more visibility and the chronic effects are often neglected and not clearly understood. The need for developing studies to emphasize chronic (long-term) effects of crude oil on marine biota was the substance of a recent conference (ref. 18).

The sublethal effects of oil require added investigations. Some petroleum fractions tend to block organs of chemoreception in certain marine crustaceans (ref. 19). Petroleum hydrocarbons can influence reproductive activity of marine animals by masking the chemical activity of pheramones that aid in the mating behavior. The physiological implications of petroleum contamination deserve an increased research effort since our knowledge is limited as to the influence of buildup of hydrocarbons on essential biochemical cycles involving complex enzymatic systems (ref. 20).

Table 3. Petroleum hydrocarbon levels in water, sediment, plants, and animals in marine environment (selected examples)

No.	Material	Quantity	Source
1.	Sediment, West Falmouth Massachusetts	12,400 ppm (dry wt.)	ref. 14
2.	Sediment, Chedabueta Bay, Canada	0-6.8 ppm (dry wt.)	ref. 12
3.	Sediment, Narragansett Bay, Rhode Island	50-3560 ppm (dry wt.)	ref. 15
4.	Water, Louisiana coast	0.63 mg/l	ref. 16
5.	Water, Gulf of Mexico	0.33 mg/l	ref. 16
6.	Plankton, Louisiana coast	100 ppm (wet wt.)	ref. 16
7.	Sargassum plant & animals, Sargasso Sea	1-34 ppm (wet wt.)	ref. 17
8.	Fish liver, Georges Bank, New England	519 ppm (wet wt.)	ref. 15

Chronic contamination by petroleum can occur not only in areas of spills but also in the vicinity of refineries, ports, and drilling sites. In the recent years, laboratory studies have been performed to monitor the accumulation and release of petroleum hydrocarbons by marine clams, oysters, shrimps, and fishes. It has been shown that hydrocarbon is usually incorporated with lipids in gallbladder and nervous tissue which contain lipid-rich membranes (ref. 21).

The effect of Louisiana crude oil in a dosage level as high as 2,500 ppm on the respiration of oyster Crassostrea virginica was investigated in the Offshore Ecology Investigations (ref. 22). The rate of respiration was not altered to any significant level in the oysters exposed to prolonged crude oil contamination (figure 7). This animal is a filter-feeding organism and is known to accumulate hydrocarbon when exposed to low concentrations of fuel oil (ref. 23). These experimental oysters attained total hydrocarbon levels as high as 335 ppm.

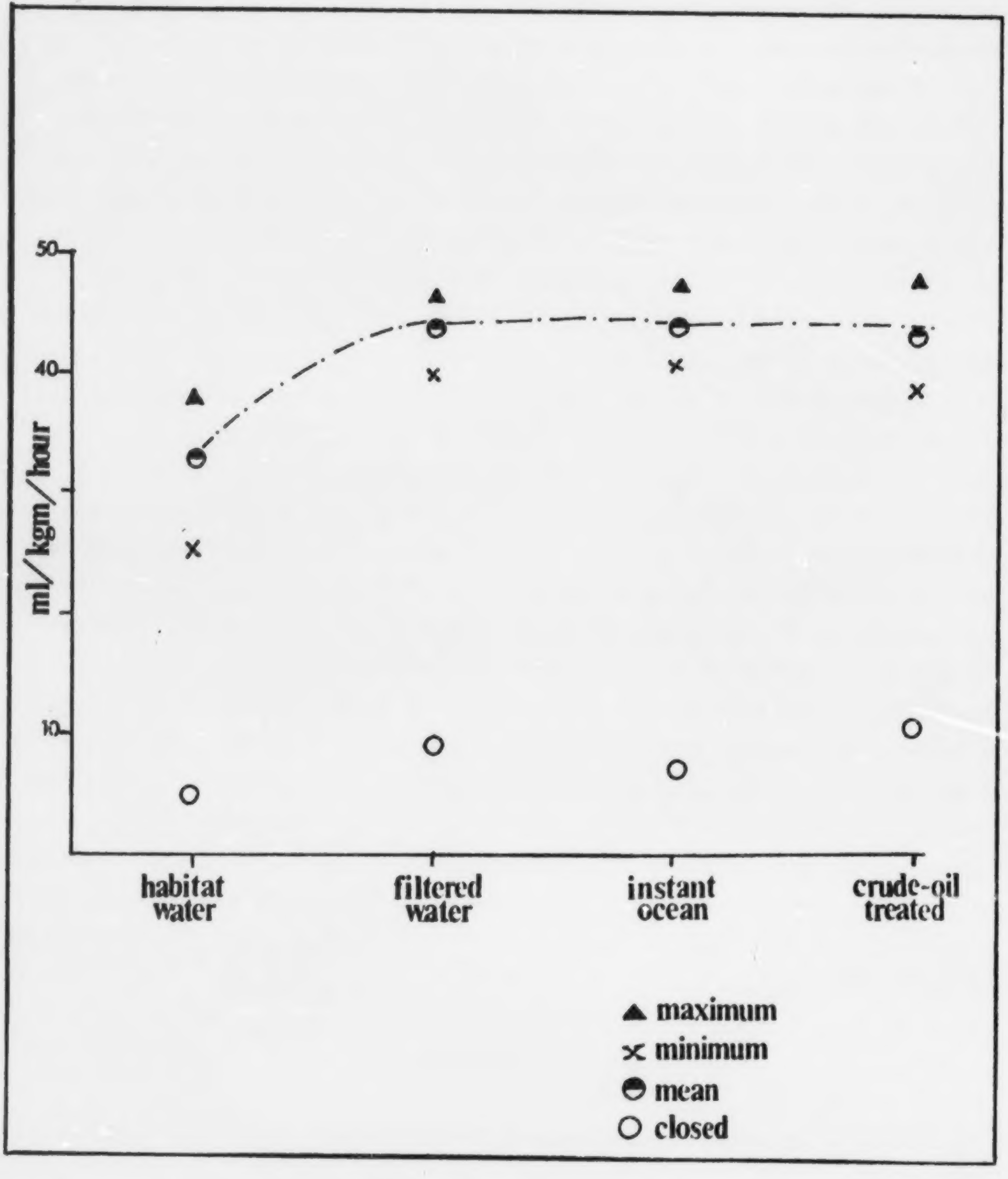

Figure 7. The oxygen uptake of oyster-biocoenoses in different experimental media including habitat water, filtered seawater, synthetic seawater and crude-oil treated seawater (2,500 ppm). Salinity of all media maintained at 32.8 parts per thousand (°/°°) and temperature at 27.5° ± 0.5°C. Note the low respiration level when the oysters remain in closed conditions.

It must be emphasized that these organisms have the inherent ability to release the accumulated hydrocarbons in favorable ambient conditions. Recent research reveals that these contaminated animals can release 90 percent of the accumulated hydrocarbons (ref. 24). Petroleum derived hydrocarbons are seen in various marine animals at levels such as 100-200 ppm for mollusks, 75-250 ppm for crustaceans, 75-250 ppm for fishes (ref. 25). It is still not understood whether this level will be retained or magnified in the food chain when transferred from one trophic level to another. It is now necessary to ask the question: What physiological or metabolic effects does the accumulated hydrocarbon or the chronic exposure of hydrocarbon impose on the organism?

In the studies on oysters, metabolic inhibition was not encountered. On the contrary, it was found that water soluble extracts of #2 fuel oil lead to reduction in oxygen consumption of Mytilus edulis (ref. 26). In a different study on mussels, increase in oxygen uptake after exposure to certain concentration of oil was reported (ref. 27). These results do not provide any definite answer on the effects of hydrocarbon on the physiological activities of these test animals. The most important aspect revolves on the understanding of not only metabolic behavior, but the ability of these test animals to grow, reproduce, and produce a progeny of normal or altered physiological traits. This aspect requires long-term studies of organisms from F_1 to F_2 generation under controlled conditions. There are suggestions that the effect is essentially physical in nature because of the apparent association of hydrocarbons with different biological membranes (ref. 19). No doubt, standardized chronic studies should be conducted to obtain answers to several unanswered questions on the effect of hydrocarbons on the marine biota.

ACKNOWLEDGMENT

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DISCUSSION

MR. DONALD W. SOLANAS (U.S. Geological Survey, Metairie, Louisiana): This is a comment, again, not a question.

Oil-base muds are not allowed to be used in the Gulf of Mexico on the Federal leases. Oil-base muds can be used in isolated problem conditions inside of a well. For instance, when a drill pipe is stuck and they are trying to free it, they are permitted in that instance to change their system into an oil-base system in order to free the pipe.

No oil is allowed to be dropped into the Gulf of Mexico on drill currings. Any drill cuttings that have any contaminants on them that are harmful to marine life or to human life must be treated, to rid them of oil or contaminants before they are allowed to be disposed of off of the platforms.

MR. JAMES B. JOHNSTON (Bureau of Land Management, New Orleans, Louisiana): Dr. George, did you reoccupy your stations after drilling was completed to see if there way any fouling growth or reoccurrence of fouling growth?

DR. GEORGE: Are you asking about reoccurrence of fouling growth?

MR. JOHNSTON: Yes. What I mean is, when you removed the plates during the drilling operation and the organisms had been destroyed, did you go back after drilling had been completed and put the plates back down to see if normal growth occurred? If so, how long did it take for normal growth to occur?

DR. GEORGE: This kind of inquiry we have not conducted yet, although we have gone four times within a year to do a survey of the fouling. And, in fact, the fouling growth of certain organisms can indeed occur even under turbid conditions.

MR. PAT M. WENNEKENS (Alaska Department of Fish & Game, Anchorage, Alaska): I would like to get a perspective. What do you call oil? How do you define it in your experiments? What do you define as oil? I mean, total oils, solution, suspension?

DR. GEORGE: You know that oil--crude or diesel or fuel oil--is such a complex mixture of various hydrocarbons with low molecular weight and high molecular weight. In fact, there are a number of things I have deliberately not touched upon with reference to the oil definition because that is not my specialty. I have also not gone into the various components of the drilling mud. So in my studies and what I am reporting today, I am referring to the composite effect of oil, as such, and not components of the oil or selected hydrocarbons of the oil.

ENVIRONMENTAL IMPLICATIONS OF SEDIMENT BULK ANALYSIS TECHNIQUES FOR TRACE METALS IN OFFSHORE WELL-DRILLING OPERATIONS

J.G. Montalvo, Jr., Ph.D., and M.M. McKown*

Abstract

The pollution potential of trace metals in chemicals used in offshore well-drilling operations can be monitored by measuring the trace metal levels in bulk seabottom sediment samples underlying well-drilling operations. Elevated trace metal levels in the surficial sediments during well-drilling operations may indicate a pollution problem. However, in the determination of trace metal levels in the sediments, the type of analysis (partial or total) must be selected. A partial (differential) analysis determines < 100 percent of a trace element in the sediment; a total analysis determines 100 percent. Trace elements are present in various chemical forms *and* locations *in sediments. The chemically unstable forms may become bioavailable as a result of various physical, chemical, and biological interactions. Stable forms, such as that fraction of trace metal in the inner layer positions of clay materials, are essentially unavailable to biota. Total digestion might therefore "overestimate" the metal levels of interest and falsely predict a pollution problem. Conversely, the total metal level may remain the same, but the fraction of an unstable form could increase in which case the problem will not be revealed without employing the partial analysis procedure. Partial analysis is currently achieved via selective extraction techniques. Unfortunately, trace metal data obtained from different types of partial digestion attack are not wholly comparable, and a need exists to standardize and validate the digestion procedure.*

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INTRODUCTION

One of the existing techniques for monitoring the pollution potential of trace metals in chemicals used in offshore well-drilling operations is to measure the metal levels in underlying seabottom sediments before and during well-drilling operations. The trace metal levels in the surficial sediments before drilling commences are indicative of background or base line levels. Trace metal concentrations in the sediments obtained at drilling sites should reflect base line metal levels plus the contributions, if any, of trace metals derived from the well-drilling operations. Various mechanisms may contribute to the transfer of a trace metal fraction from a well-drilling operation to the receiving bottom sediment. Solid particulates in drill cuttings and well-drilling fluids may be washed from the derrick floor and walkways during rainfall and maintenance operations, and consequently may migrate to the sediment under and around the rig site. Spillages of drilling muds may occur while the mud is being pumped into chemical containers aboard the offshore drilling rig or while the mud is being pumped into a barge tied up alongside the rig. Discharges of drill cuttings contaminated with oil well-drilling fluids may also contribute to elevated trace metal levels in the surficial sediments around a rig site.

If the trace metal levels in the sediments obtained during well drilling operations are elevated above base line levels, further chemical analyses of samples of oil well-drilling fluids, drill cuttings, paint chips from the rigs, oil wipe samples, etc., are necessary before it can be stated with any degree of accuracy that the increased metal levels originated from chemical use in well-drilling operations.

In obtaining surficial sediment samples for trace metal analysis, usually the volume or mass of sample obtained is quite large (i.e., bulk analysis) and may contain up to one cubic foot of sample (ref. 1). In the laboratory, a subsample of several hundred grams is taken from the bulk sample and mixed well. The actual chemical analysis is performed on 1 to 4 grams of sample.

The identification of trace metals that have in the past or are currently being added to chemicals used in well-drilling operations is no easy task due to the proprietary nature of the formulations. Chemicals are used in drilling muds for various purposes: to control pH, bacteria, corrosion, emulsion flocs, foams, drilling-fluid circulation, and reservoir-rock permeability. Although drilling fluids contain primarily clays and weighting agents such as barium sulfate, a search of the readily available patent literature through 1963 has revealed that many different inorganic salts and compounds have been added to chemicals used in well-drilling operations, as shown in the shaded areas of figure 1 (ref. 2). Furthermore, consideration only of the "heavy metal" suite implies that the primary concern is with "trace metal" analysis and that the alkali and alkaline earth metals are excluded (ref. 3). Several of the latter are important from the pollution standpoint (beryllium, for example). Therefore, the term "trace metal" as used here will refer to low concentrations in the hydrosphere in the μg/l range (ppb) of the heavy metals such as Cr, Ni, Cu, Cd, Hg, Pb, As, etc., and alkaline earth metals such as Be, etc.

Scientists charged with assessing the environmental impact of trace metals in sediments in conjunction with well-drilling operations should understand fully the environmental implications of such bulk analysis data based on the merits and limitations of the analytical procedures. The mere presence of a trace element constituent in the sediment during well-drilling operations neither indicates nor predicts the nature and significance of adverse effects to the aquatic organism. A literature search on this subject clearly demonstrates a lack of knowledge of the impact (acute and chronic) of drilling fluid components on marine biota. Therefore, the trace metal data supplied should differentiate that fraction of a given trace metal that is potentially bioavailable from that which is not in order to properly estimate environmental impact. An examination of the basic analytical procedures used for sediment bulk analysis for trace metals in offshore well-drilling operations is reviewed here pertinent to environmental considerations. Since there are gaps in the basic analytical procedures, and since the procedures are nonetheless currently being applied, there appears to be justification for extensive research.

THEORY OF BULK SEDIMENT ANALYSIS*

Before the control mechanisms for trace metals in surficial sediments associated with well-drilling operations are considered, chemical parameters important in sediment bulk analysis for trace metals need to be introduced. Table 1 shows several important parameters to be considered in developing the sampling program. Under socioeconomic considerations, variables such as cost, rapidity, and simplicity are important. The cost must not be prohibitive, otherwise an insufficient number of samples will be included in the sampling program. Rapidity refers here to the sample turnaround time. Simplicity implies a minimum number of steps in the analytical procedures since each sample manipulation increases the probability of contamination of the original sample. Consequently, trends in trace metal analysis in sediments have been towards methods requiring smaller sample sizes and minimum concentration procedures while retaining

Table 1. Parameters important in sediment bulk analysis

Socioeconomic	Chemical	Environmental
Cost	Sensitivity	Validity
Rapidity	Precision	
Simplicity	Accuracy	

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*This paper is concerned with bulk sediment analysis in conjunction with chemical use in offshore well-drilling operations; many of the principles presented can be applied per se to other environmental applications of sediment bulk analysis of trace metals.

high sensitivities (refs. 4,5). Pertinent chemical parameters are sensitivity, precision, and accuracy. Background concentrations of total trace metal levels in sediments and soils may vary from 0.03 to 100 ppm (refs. 6-8). The technique must adequately detect background levels of trace metals and must concurrently obtain a minimally acceptable signal-to-noise ratio. The precision and accuracy of the analytical method cannot be overemphasized and must also be optimized since the number of samples required decreases with increase in precision and accuracy. Validity of the procedure refers to the proposed definition of the fraction of trace metals in the sediment that is bioavailable.

The processes of transport, distribution, and removal of marine sediments are part of the biogeochemical cycle. Trace metals enter natural water systems by normal weathering of rocks or are added as a result of man's activities. Whenever the rate of input of trace elements into offshore waters or surficial sediments exceeds the natural rate of cycling, contamination with adverse ecological effects may result (ref. 9).

Potential perturbation of the biogeochemical cycle (of Rubin, ref. 9) at specific points due to well-drilling operation is shown in figure 2. A more detailed schematic of well-drilling operations in relation to surficial bottom sediments is shown in figure 3. The water column contains dissolved trace metals and other nonmetallic constituents, suspended solids, and aquatic organisms. Particulate matter and dissolved constituents from well-drilling operations may enter the hydrosphere, inducing several complex reactions. A large number of phenomena will exert varying effects on the transfer of trace metals from the well-drilling operations to the bottom sediments. The solid particles (drill cuttings and oil well-drilling fluids) may drift downward through the water column to the seabottom. During this transport of solid particles in the hydrosphere, rapid ion-exchange processes may take place, effecting movement of dissolved constituents from the water column to the

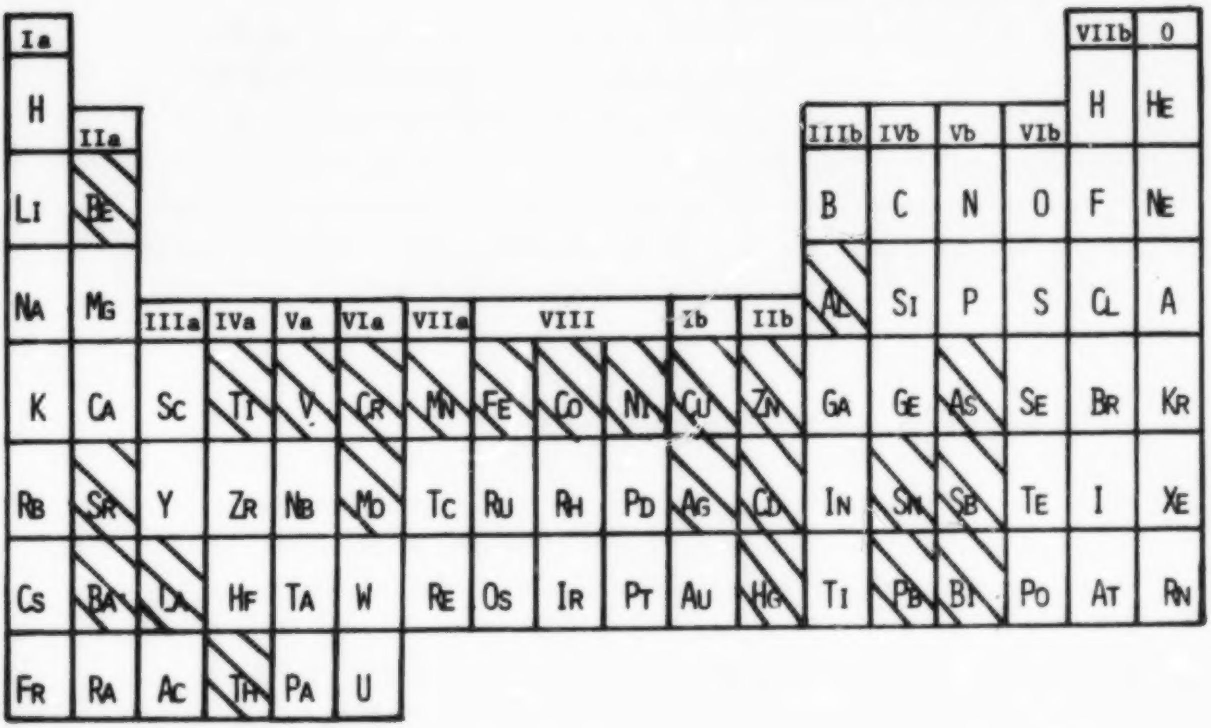
Ia
IIa
IIIa
IVa
Va
VIa
VIIa
VIII
Ib
IIb
IIIb
IVb
Vb
VIb
VIIb
0
H
He
Li
Be
B
C
N
O
F
Ne
Na
Mg
Al
Si
P
S
Cl
A
K
Ca
Sc
Ti
V
Cr
Mn
Fe
Co
Ni
Cu
Zn
Ga
Ge
As
Se
Br
Kr
Rb
Sr
Y
Zr
Nb
Mo
Tc
Ru
Rh
Pd
Ag
Cd
In
Sn
Sb
Te
I
Xe
Cs
Ba
La
Hf
Ta
W
Re
Os
Ir
Pt
Au
Hg
Tl
Pb
Bi
Po
At
Rn
Fr
Ra
Ac
Th
Pa
U

Figure 1. Trace elements known to have been added to chemicals used in well-drilling operations.

particles or vice versa. The interstitial water may also undergo rapid exchange of chemical constituents with the surrounding hydrosphere. In addition, suspended solids in the water column might be adsorbed onto the solid particles from the well-drilling operations. The nature of the solid particles could induce adsorption of dissolved constituents from the surrounding environment.

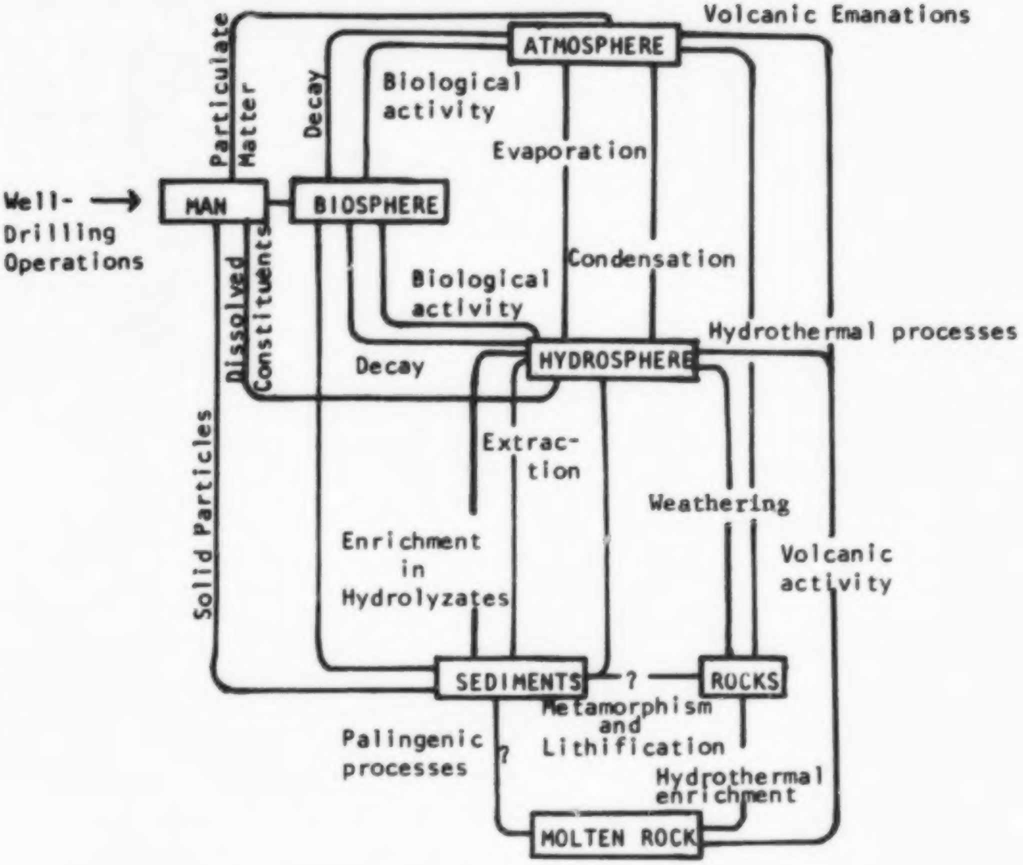
Volcanic Emanations
ATMOSPHERE
Particulate Matter
Decay
Biological activity
Evaporation
Well-Drilling Operations
MAN
BIOSPHERE
Dissolved Constituents
Condensation
Biological activity
Hydrothermal processes
Decay
HYDROSPHERE
Solid Particles
Extraction
Weathering
Enrichment in Hydrolyzates
Volcanic activity
SEDIMENTS
?
ROCKS
Metamorphism and Lithification
Palingenic processes
?
Hydrothermal enrichment
MOLTEN ROCK

Figure 2. Biogeochemical cycle of trace metals in nature with major input points of man's activities during offshore well drilling operations (from Rubin, ref. 7).

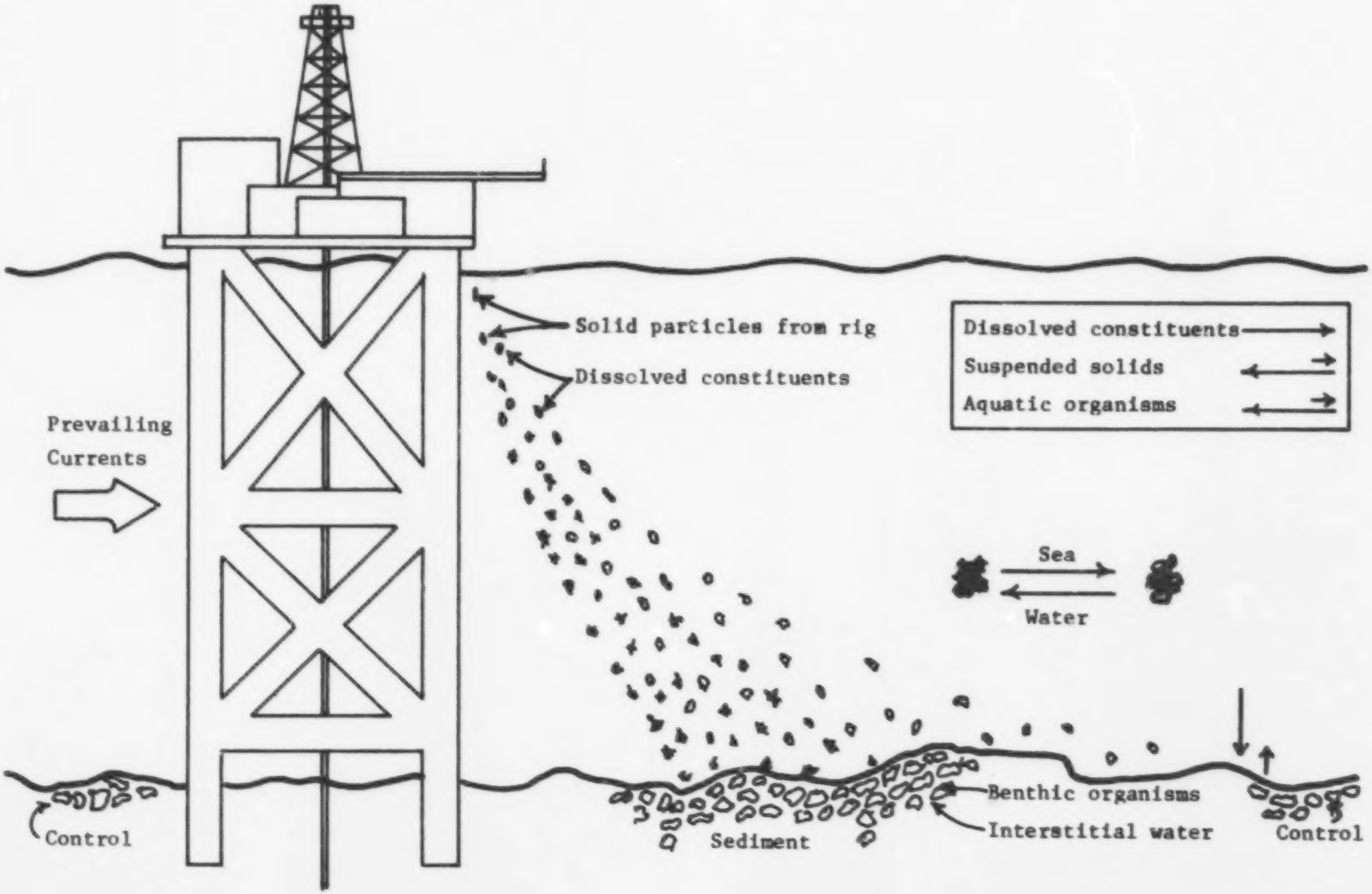
Solid particles from rig
Dissolved constituents
Dissolved constituents
Suspended solids
Aquatic organisms
Prevailing Currents
Sea
Water
Benthic organisms
Interstitial water
Control
Sediment
Control

Figure 3. Schematic of well-drilling operation in relation to surficial bottom sediments.

The solid particles may be adsorbed onto the surface of aquatic organisms or be ingested as a source of food. The dissolved constituents from the well-drilling operations will primarily be diluted to seawater background levels.

Ultimately, the solid particles that have undergone variable chemical, physical, and biological modifications will settle on the surficial sediments around the rig site.

It is generally accepted that sediments are scavengers of trace metals; suspended solids and aquatic organisms can also concentrate trace metals (refs. 10-12). Therefore, trace metal "sinks" in the marine environment include sediments, suspended solids, and aquatic organisms. Trace metal levels in seawater are low due to the large dilution factor and transfer of metal to the "sinks". Bottom sediments may be a sink for trace metals originating from chemicals used in well-drilling operations. Sediments are relatively nontransitory in nature and are also known to serve as a habitat for a large and complex community of biological organisms collectively known as the benthic community. Therefore, sediment sampling and analysis should be included in comprehensive plans to study environmental aspects associated with well-drilling operations.*†

In order to determine the effect of exposing surficial sediments to chemicals associated with well-drilling operations, the chemical form and location of the contaminants within the sediments must be known.

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*Enrichment of certain trace metals in surficial sediments may also occur due to deposition of suspended matter from the water column not associated with drilling operations, by diffusion from deeper layers of the sediments, or by redistribution through hydrodynamic processes. It is assumed in sediment studies during well-drilling operations, that through the use of control samples, any significant naturally occurring enrichments will be negated.

†There may also be variations in metal levels with depth of sediments; for this reason, sediment surficial samples are always taken at the same depth.

A trace metal contaminant or constituent associated with well-drilling operations can exist in the natural environment, and these species may vary from chemically unstable to extremely stable compounds or complexes. The chemically unstable forms in the sediment layer, from the sediment itself and from well-drilling contaminants mixed with the natural sediment, are subject to active migration into the biological food web and may range from highly ionizable species to soluble, readily available organic complexes. On the other hand, the stable chemical forms may range from highly insoluble inorganic precipitates, complexes, compounds, and minerals to very nonreactive organic complexes. The chemically stable and usually nonreactive forms constitute the major fraction of most natural sediments and rarely enter into the biological cycle. The chemical form of the trace metal contaminant can affect both its relative toxicity and its availability to influence biological communities.

The location of chemical constituents within the sediments also determines the availability of these constituents to biological communities. The chemical constituents are located within the sediment in a variety of positions. Physically, sediments are comprised primarily of soil materials such as clays, silts, sands, etc., and interstitial water (IW) (ref. 13). Chemically, sediment contains a majority of the chemical elements.

Table 2 shows the more important chemical constituent locations in sediments (refs. 13-23), trace metal forms, and bioavailability of the trace metal forms in the various sediment locations. Chemically, constituents in Phase (I)* and its associated trace metal forms have the most immediate effect on changes in the water column; trace metal fractions in Phase (II) may have a longer term effect on water quality by

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*The assumption is made that chemically unstable forms in sediments are potentially bioavailable. A sediment phase consists of a location and the chemical forms in the location.

Table 2. Sediment chemical constituent locations, forms, and bioavailability

	Chemical constituent location	Trace metal forms	Bioavailability	Comments
I.	Dissolved or disassociated in the sediment interstitial water (IW)	Oxidized and reduced forms of trace metals; trace metal chelates	Yes	IW--up to 50% of the volume of a sediment; contains only 0.1 to 10% by weight of total chemical constituency of a sediment
II.	Absorbed (ionically bound) to charged mineral and organic surfaces (exchangeable)	Since this sediment location is anionic in nature, mobile cations predominate such as trace metals	Yes	1 to 20% by weight of total chemical constituency
III.	Oxides, hydroxides, and hydrous oxides of manganese and iron that exist as particulate coatings or discrete particulates	This sediment fraction exists as a redox phase; trace metals known to be entrapped in these coatings under formation (oxidizing) conditions and released under reducing (dissolution) conditions	Yes	Up to 50% by weight total Fe & Mn found in this sediment location
IV.	Those chemicals that are associated with or are an integral part of the sediment organic fraction	Metal-organic forms that vary in stability from immediately bioavailable to resistant to decomposition	Yes	Organic portion of sediment seldom exceeds 10% by weight of total chemical constituency
V.	The residual phase	Trace metal in the inner layer portions of clay minerals or within the mineral crystalline lattice	No	Up to 75% or more by weight of total concentration of most chemical constituents in a stable, unavailable form.

acting as a reservoir for constituents that are removed from the IW. Phase (III) trace metals may be released to the water phase during reducing conditions. Phase IV trace metal materials may be incorporated into the food web or migrate to the aqueous phase with potential for long-term effects depending on the nature and degree of microbial degradation. Phase IV materials might also act as scavengers of some trace metals. Phase V materials are considered biologically inert.

Various mechanisms have been suggested whereby trace metals in sediments may interact with biota: (a) particulate ingestion of sediment matter suspended above the seabottom, (b) particulate ingestion in the sediment layer, (c) ingestion of food material in and above the sediment layer, (d) complexation by biological chelating agents, (e) incorporation into physiological systems, and (f) ion exchange and sorption on tissues or membrane surfaces (refs. 24-26). All of these mechanisms imply a degree of bioavailability of the various trace metal forms in a sediment. Clearly, an inert trace metal form in a sediment might be expected to pass unchanged through the digestive tracts of biota; for example, trace metals within insoluble mineral crystalline lattices.

The analytical chemist performing the trace metal analysis of surficial sediments in conjunction with the environmental aspects of chemical use in well-drilling operations must determine whether a total analysis for specific trace metals is desirable. A partial (differential) analysis is intended to determine < 100 percent of a trace element in the sediment; a total analysis determines 100 percent of a trace element in a sediment.

It is necessary to explore the environmental significance of partial vs. total analysis data given to biologists. Assume that only the five phases of trace metals in a sediment, as shown in table 2, are present in significant concentrations. Let the total concentration of a given trace metal (M) in Phase I be represented as,

$$\sum_{r=1}^{n} (\text{Phase I})_r = (\text{Phase I})_1 + (\text{Phase I})_2 \ldots (\text{Phase I})_n \qquad (1)$$

where each (Phase I) term represents the concentration of a particular form of trace metal M in Phase I location. The equation representing the total concentration of trace metal M in all five phases of the sediment is given by M_T,

$$M_T = \sum_{r=1}^{n} (\text{Phase I})_r + \sum_{r=1}^{n'} (\text{Phase II})_r + \sum_{r=1}^{n''} (\text{Phase III})_r \qquad (2)$$

$$+ \sum_{r=1}^{n'''} (\text{Phase IV})_r + \sum_{r=1}^{n''''} (\text{Phase V})_r$$

Let the concentration of chemically unstable trace metal (M) in Phase I be represented as,

$$\sum_{s=1}^{n} (\text{Phase I})'_s = (\text{Phase I})'_1 + (\text{Phase I})'_2 + \ldots (\text{Phase I})'_n \qquad (3)$$

where each (Phase I)' term represents the concentration of a particular form of trace metal M in Phase I that is bioavailable. The total concentration of bioavailable trace metal M in all five phases of the sediment is therefore given by M_B,

$$M_B = \sum_{s=1}^{n} ((\text{Phase I})'_s + \ldots \sum_{s=1}^{n''''} (\text{Phase V})'_s \qquad (4)$$

The fractional limits of bioavailable trace metal M_B in the sediment in relation to M_T can be given by:

$$0 < \frac{M_B}{M_T} < < 1 \qquad (5)$$

or

$$0 << \frac{M_B}{M_T} < 1, \qquad (6)$$

depending upon the identity of M, etc.

If M_B/M_T approaches 1, then the analyst is justified in performing a total analysis. On the other hand, if M_B/M_T is significantly less than one, then the analyst will "overestimate" the value of an element that is bioactive if a total analysis is performed. Values obtained for M_B/M_T will depend on the extraction media employed for partial analysis. For example, values of M_B/M_T of < 0.5 were generally obtained using dilute HNO_3-HCl; H_2O_2; and HOAc with $NH_2OH \cdot HCl/H_2O_2$ for partial analysis of sediment from three geographical areas (table 3).

The environmental implications of sediment bulk analysis techniques for trace metals in offshore well-drilling operations are schematically represented in table 4. Clearly, if the total metal level increases relative to the control values (the metal levels of interest), the unstable forms which may become bioavailable as a result of various physical, chemical, and biological interactions, might be "overestimated." A pollution problem would thus be falsely predicted. In such a case the true interpretation of the data is possible only with partial analysis. Conversely, the total metal level might remain essentially the same but the fraction of an unstable form could significantly increase, in which case environmental impact will not be revealed. Currently some environmentalists tend to request "total" values for an element on the assumption that all the trace metal in the sediment sample is bioavailable.

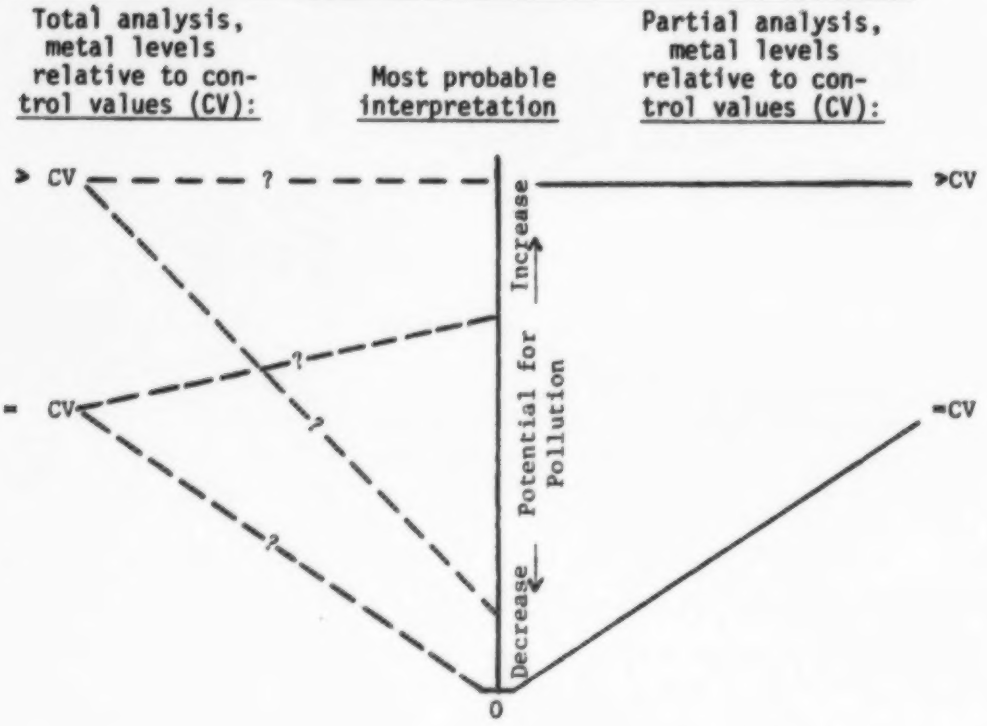
Table 3. Reported values for M_B/M_T in sediments

Sediment source	Partial digestion technique	Trace metal	M_B/M_T (%)	Ref.
Offshore southwest Florida	Leach with hot HNO_3-HCL, 0.14M and 1.09 M, respectively	Cu	12	27
		Cr	42	
		Fe	75	
Puget Sound	H_2O_2	As	<10	28
		Sb	<10	
	Oxalate	As	66	
		Sb	48	
	Citrate-dithionite-bicarbonate	As	34	
		Sb	31	
Saanich Inlet, British Columbia	25% HOAc plus 0.25M $NH_2OH \cdot HCl$; separate residue, leach with 30% H_2O_2	Co	15	29
		Mo	44	
		Li	18	
		Sr	29	
		Fe	11	
		Mn	22	
		Ni	21	
		Cu	58	
		Zn	40	

The total trace metal content in sediment samples, 100 percent, can be determined using emission spectrography, X-ray fluorescence, or neutron activation analysis; it can also be determined after complete digestion or fusion.

In partial or differential analysis, the sediment sample digestion or extraction technique is designed in such a manner as to remove Phase I - Phase IV elements from the sediment residue. Many different procedures have been employed in partial analysis (refs. 26,30,31,32), as shown in table 5. Certain experiments, described in the following section, were conducted in this laboratory to show that the sediment trace metal results obtained from different types of partial digestion attack give valuable information about the nature of the unstable chemical forms.

Table 4. Environmental implications of sediment bulk analysis techniques for trace metals in offshore well-drilling operations based on partial vs. total analysis


Total analysis, metal levels relative to control values (CV):
Most probable interpretation
Partial analysis, metal levels relative to control values (CV):
> CV
?
= CV
?
?
?
Increase
Potential for Pollution
Decrease
0
>CV
=CV

Insufficient sediment bioassay studies have been completed to date to indicate unequivocally all of the chemically unstable forms of trace metals in sediments which are bioavailable and which hence may act as potential pollutants (ref. 14). A major problem in conducting and interpreting long-term bioassay tests of offshore sediments is caused by the differences in the hydrodynamics of the test conditions as compared to the hydrodynamics in deep or offshore waters (ref. 33). A controlling factor influencing the availability of trace metals to biota in deep

Table 5. Partial digestion techniques reported in the literature

Technique	Composition of digestion mixture
Cold extraction	Buffers; variety of dilute acids (e.g., nitric, hydrochloric, acetic, EDTA, etc.); mixtures of weak acids plus reducing agents.
Hot extractions	An individual acid (e.g., HNO_3) or a mixture of acids (e.g., aqua regia, nitric-perchloric, etc.); hydrogen peroxide.
Fusions	Acid ($K_2S_2O_7$ or $KHSO_4$, etc.); alkaline (Na_2CO_3, KNO_3, Na_2O_2, and NaOH, K_2CO_3, and Na_2CO_3, etc.).
Others	Dry ashing.

waters is the hydrodynamics of the mixing of the sediments and the interstitial water associated with the sediments and the overlying waters.

Thus, bulk analysis of the sediments for trace metals should supplement greatly the bioassay test results. But the chemist performing the analysis must realize that bottom sediments are not simply a wet sample of soil, since soil and bottom sediments are formed under different conditions (ref. 23). Bottom sediments are normally subject to reducing conditions except at the zone of contact with the aqueous phase, whereas soils are usually formed under aerobic conditions. Further, sediments contain higher amounts of organic matter than soils and also are not subject to the leaching processes as are soils. Finally, techniques for trace metals in terrestrial soils were developed for geochemical exploration and studying availability of the metals by plants. Extrapolation of these soil techniques to sediments for environmental purposes may not be entirely valid.

EXAMPLE OF A PARTIAL ANALYSIS TECHNIQUE

Table 6 shows the current EPA (region IV) recommended procedure for partial digestion of trace metals in sediments. The procedure is simplification of a previously recommended multistep bulk sediment analysis procedure (ref. 1). The final concentrations of HNO_3 and HCl after addition of the water are 0.14M and 1.09M, respectively. This acid mixture is mildly acidic and also could be considered a mild oxidant depending on the temperature. That fraction of a trace metal in a sediment which might be expected to be leached from the sample in this solution would include trace metal in the following forms: soluble salts, absorbed, an iron-manganese phase, sulfides, and organics (ref. 30).

No experiments have been reported in the environmental literature where a partial digestion technique employing a given $HCl\text{-}HNO_3$ mixture to leach trace elements from sediments has been studied as a function of temperature and time of digestion; therefore, such a study was performed

Table 6. An EPA-recommended partial digestion (Leaching) technique for trace metals in sediments

ENVIRONMENTAL PROTECTION AGENCY
REGION IV, SURVEILLANCE & ANALYSIS DIVISION
CHEMICAL SERVICES BRANCH

TENTATIVE DIGESTION OF SEDIMENTS FOR METAL ANALYSIS

June 28, 1973

1. Weigh 1-2 g of dry (103°C) sediment into a 250 ml Erlenmeyer flask.
2. Add 50 ml of water, 0.5 ml conc. HNO_3 and 5 ml conc. HCl.
3. Heat at 95°C for 15 minutes.
4. Cool and clarify the sample by filtering or centrifuging.
5. Dilute to 100 ml.
6. Proceed with atomic absorption analyses for trace metals, such as: Pb, Zn, Mn, Cd, Cu, Ni, and Cr.

in Gulf South Research Institute laboratories. Separate portions of sediment samples obtained from a well-mixed bulk sediment sample* were digested at 35°, 65°, or 95°, for periods ranging from 15 to 180 minutes and analyzed for Cu and Ba (figures 4 and 5) and Cd, Pb, Cr, Fe, and V. A reflux condenser was used at 95°C to prevent loss of water or acid. The digestion process was quenched by immediate filtration, and extracts were analyzed by atomic absorption spectrometry.

The general shape of the kinetic curves in figures 4 and 5 illustrates the variables involved in partial analytical techniques for trace metals in sediments. The recommended 15-min digestion period is apparently sufficient for extracting some of the metals but not all. The shapes of both curves are similar; the plateaus indicate when a given chemically unstable form(s) is removed from the sediment. The digestion temperatures were varied in increments of 30°C (i.e., 35° → 65° → 95°). Striking differences are apparent in the dependence of the level of metal recovered as a function of temperature; for Cu, at least three different chemically unstable trace metal forms in the sediment are suggested (ref. 25). On the other hand, Ba does not show a dependence of metal recovered as a function of temperature in the range 33° to 95°C; therefore, at least one unstable form of metal is suggested (ref. 27). The data is summarized in table 7.

A full interpretation of the kinetic data is beyond the scope of this paper, but comments directed towards a generalized explanation will be given for Cu and Ba. The Cu recovered at 35°C could represent the Cu in the interstitial water and the loosely absorbed Cu (hence total of two different forms); the Cu recovered at 65°C may represent the sulfide Cu whereas at 95°C probably the organic Cu is being obtained. The

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*Collected from a drainage ditch (NASA/NSTL, Bay St. Louis, Mississippi).

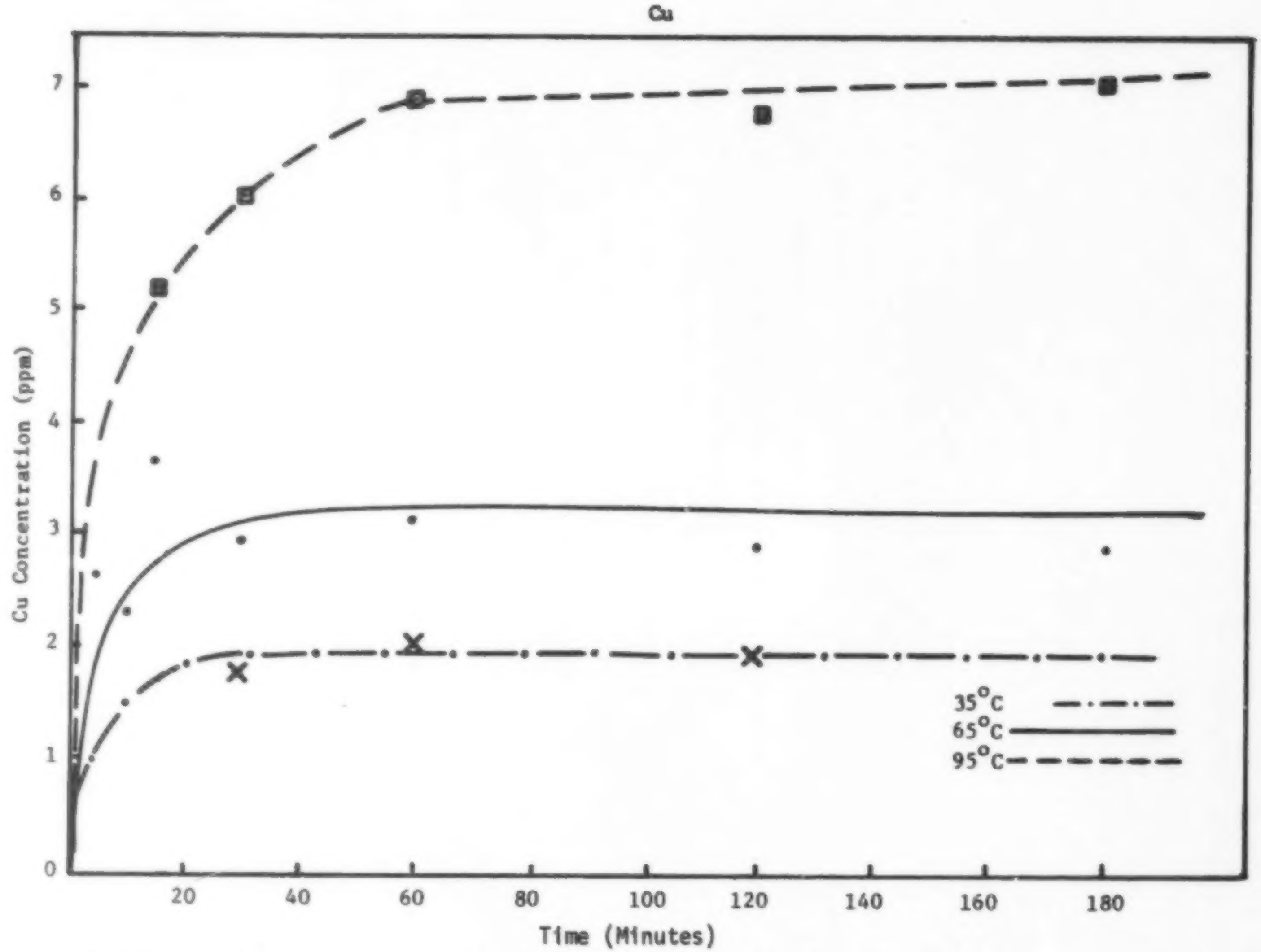

Figure 4. Diagram illustrating the effect of temperature and time of digestion on recovery of Cu from a sediment.

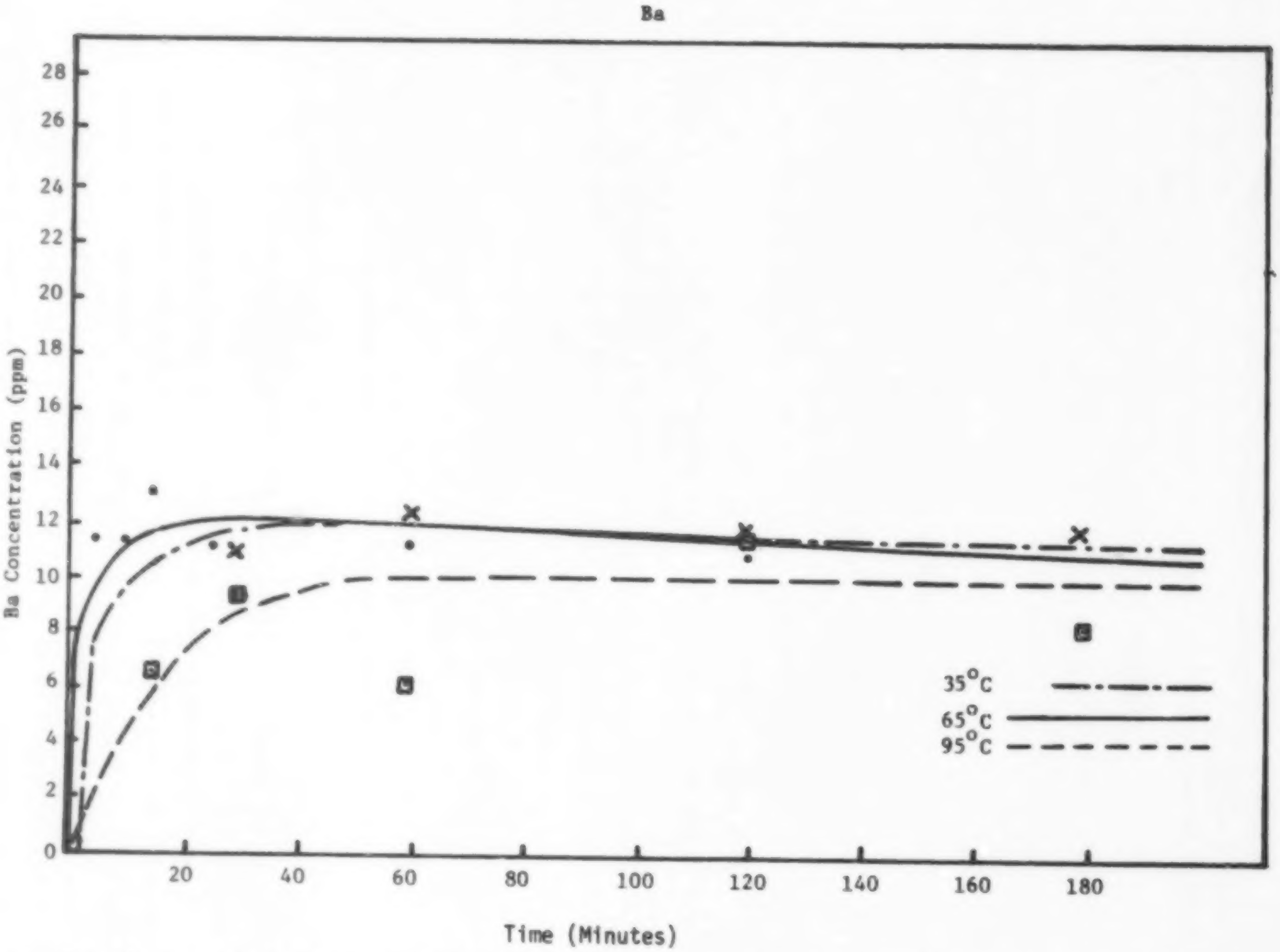

Figure 5. Diagram illustrating the effect of temperature and time of digestion on recovery of Ba from a sediment.

Table 7. Relative recoveries of trace metals and number of trace metal "forms" detected after 3 hours of partial digestion as a function of digestion at three different temperatures

Trace element	Recoveries relative to 35°C 35°C	 65°C	 95°C	Postulated minimum number of trace metal forms in the sediment
Cu	1.00	1.60	3.52	3
Cd	1.00	1.00	0.98	1
Pb	1.00	1.14	1.16	2
Cr	1.00	2.48	2.96	3
Fe	1.00	1.51	2.24	3
Ba	1.00	0.97	0.89	1
V	1.00	0.90	2.42	2

Table 8. Dependent variables in partial analytical techniques for trace metals in sediments

Digestion:
Temperature
Time
Solvent composition
Sediment mesh size
Sediment lithology

lack of further recovery of Ba at 65° and 95°C is not surprising in view of the common association of Ba with chemically unstable carbonates (ref. 27).

Other experiments have been performed in this laboratory to identify the variables involved in partial analytical techniques and their dependence on several trace metal levels recovered and, therefore, the forms of metal recovered. The variables which have been identified to date which affect the metal recovered are summarized in table 8. The need to standardize partial analysis techniques should be apparent.

SUMMARY

The rationale for sediment bulk analysis techniques to monitor trace metal pollution from the chemicals used in well-drilling operations was presented for offshore or deep-water drilling. Many of the principles developed can be applied to other environmental applications requiring sediment bulk analysis for trace metals.

Trace metal contaminants from the chemicals used in the well-drilling operations may perturb the marine sediments in the biogeochemical cycle, which can be revealed by chemical analysis for trace metal levels. However, in the determination of trace metal levels in the sediments, the type of analysis (partial or total) must be carefully considered.

The results of a kinetic study of a recently recommended EPA partial digestion technique for trace metals in sediments is presented for Cu and Ba analysis. By simple variation of the sediment digestion temperature in the partial analysis procedure, up to three different chemically unstable trace metal forms that are potentially bioavailable were postulated for various metals. Important variables in the partial analytical techniques for trace metals in sediments were also identified: composition of digestion mixture, temperature and time of digestion, sediment mesh size, and sediment lithology.

The total concentration of chemically unstable forms of a trace metal in the sediment was assumed potentially bioavailable (M_B) and is related to the total concentration of the metal in the sediment (M_T) by

$$0 < \frac{M_B}{M_T} < 1 .$$

Values for M_B/M_T, while dependent on a specific partial analysis technique, appear in general to be <0.5. The environmental implications of sediment partial vs. total analysis in conjunction with chemical use in well-drilling operations suggests that the partial and not total analysis technique be utilized in the environmental survey (ref. 35).

There are obvious needs to identify the trace elements present in the modern chemicals used in well-drilling operations, to standardize

Table 9. Need for improved sediment bulk analysis methodology for environmental monitoring and control in offshore well-drilling operations

Needs	Suggested approach	Comments
1. Identify trace metals in chemical use in modern well-drilling operations	Qualitative multi-element analysis of commercial chemicals followed by quantitative analysis	This may necessitate ongoing studies
2. Standardize partial analysis techniques from existing technology	Should look to EPA for recommendations since this regulatory agency has most experience in the field	Immediate need for standardization in offshore areas currently undergoing well-drilling operations; standardization efforts already underway
3. Develop more optimized partial analysis procedure leading to improved specificity in quantitating various forms of trace metals in sediments for future standardization	Solvent extraction techniques; differential thermal analysis; separate magnetic and nonmagnetic fractions; mineralogy studies; electron microprobe	Direct application in sediment bioassays and in modeling biopathways

partial analysis techniques to cope with current offshore studies, and to develop better partial techniques for future standardization. Reasonably specific partial analysis techniques for identifying and quantitating the various chemically unstable forms of trace elements in sediments could have direct impact on sediment bioassay studies. Table 9 summarizes, for ease of referral, suggested areas of research to improve sediment bulk analysis methodology for environmental control and monitoring of offshore well-drilling operations.

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DISCUSSION

MR. JACK W. ANDERSON (Texas A&M University, College Station, Texas): You may be aware that the Corps of Engineers is concerned with this problem, also, with their dredge material disposal, and that they recently funded a contract that we are working on to look at the availability of heavy metals to benthic organisms. Now, this exact type of scheme of separation, and so forth, will be used.

MR. ARTHUR J. HOROWITZ (Texas A&M University, College Station, Texas): I have got a question. First of all, you mentioned that you feel that lattice supplementals are not likely to be taken up by an organism once it has been eaten: you expect it to be excretable. And my question is, how sure are you of this? What are you using to check it?

DR. MONTALVO: Could you rephrase your question?

MR. HOROWITZ: Let us assume that you have got a polychaete living in the mud and it is chewing it up; essentially, it is going in one end and out the other. How sure are you that there is nothing being taken out?

DR. MONTALVO: Okay. We have done some experiments whereby a certain fraction of a metal in the sediment will not be removed by reflexing that sediment with concentrated nitric acid. Now, if that certain fraction of metal is not removed from the sediment with concentrated nitric acid, I hardly think that the pH in the digestive tract of an organism, or the enzymes, is capable of breaking that sediment apart and actually removing these inner layer trace metal ions. I just cannot visualize that.

If we flux our sample for, say, 3 hours with concentrated nitric acid and the metal is not removed, it is hard to convince me that the biota, which will have undoubtedly a mild acidity in the animal's digestive tract, can do this.

MR. HARWOOD: Just out of curiosity, have you tried to reproduce those results? In other words, have you taken the sediment and refluxed it once and taken another aliquat and refluxed it again? How reproducible were the results?

DR. MONTALVO: If we get into a discussion of the experimental procedure of trying to extract trace metals from sediments, one has to remember that whenever we are doing this, one of the dependent parameters in the study is time. That is to say that one has to perform a kinetic study and plot the metal level recovered versus the time. And in doing so, you will, in every instance, obtain a plateau. And all you have to do is to increase or to do your digestions or extractions for a sufficiently long enough period of time until you are on the plateau of your curve. If you do that, you will get repeatable results. If you do not do that and you stop your digestion while you are in the rising part of the curve, you will get data of very poor precision and accuracy.

DR. ELLIOT S. HARRIS (NIOSH-Cincinnati, Ohio): I think it is all well and good to look at the metals in the sediment. But what we are interested in there is the effect on the food chain and how these metals are going to move through that food chain.

Have you looked at any of the fixed biota and seen whether they contain that which you are concerned with?

DR. MONTALVO: We are also involved in a study of this nature, but I hesitate to speculate on the results of that data since it is an ongoing study and it has not reached that stage yet.

The Offshore Ecology Investigation
Slide Presentation

Joe W. Tyson*

Public awareness of the conflict existing between energy production and environmental protection has resulted in a need for the public to know and understand the impact of man's activity on his environment. The Offshore Ecology Investigation came about as a consequence of this serious need and asks this simple question: "What is the measurable impact of drilling for oil, and later producing it, on the estuarine and marine environment in our Nation's greatest offshore oil production region, the Louisiana Shelf?" (See figure 1.) To answer the deceptively simple question, the Gulf Universities Research Consortium has coordinated a 2-year Offshore Ecology Investigation.

A Project Planning Council was named and a diverse group of university, government, and industrial scientists agreed on the major outlines of a scientific program to provide an answer to the question (see figures 2 and 3). After the general guidelines were formulated, the Gulf Universities Research Consortium selected 23 principal investigator scientists to participate. They represented 13 of the educational and nonprofit institutions in the Gulf States (see figure 4). The scientists and their institutions who provided the several parts of the complete program are acknowledged, as are the members of the Agency Advisory Committee named to consider the sampling methodologies and analytical procedures (see figure 5).

Biological, chemical, and physical experiments were defined and sites were selected in Timbalier Bay, Louisiana, and offshore to about 100 feet of water (shaded in darker gray). (See figure 6.) Sampling stations adjacent to drilling or production and control sample stations (where there

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had never been oil drilling) are within the same region, thus making it possible to do valid comparative studies. All sampling stations are located far enough from the Mississippi River mouth to uniformly minimize, but not eliminate, its impact. As is seen in figure 7, a very-high-altitude National Aeronautics and Space Administration view, tremendous quantities of sediments and other materials leave this river to flow in a general westward direction with the Western Loop Current during most of the year.

A low-elevation aerial oblique view of the region, in this artist's illustration (see figure 8), indicates the variable water depth and the changing geography found as one moves from the outer shelf onto the beach and into the bay. Platforms, both for drilling and production, are quite dense in this region between Timbalier Island and Casse-Tete Island (see figure 9).

Figure 10 shows a platform just west of Philo Brice Island in Timbalier Bay, which was one of the intensive sampling sites with sample stations being located in a radial pattern outward from the platform.

The density of platforms and wells offshore is somewhat less, although recent figures indicate there are 2,650 platforms in the entire northern Gulf of Mexico (see figure 11). All of which is to say, there are hydrocarbons in this environment--whether from natural seeps, accidental spills, or as a result of overboard discharge of brine containing a few parts per million of petroleum hydrocarbons, or from other sources such as city wastes, seagoing ships, sports boats, or decay of plants and animals.

A working platform makes many contributions to the environment in addition to its physical presence (see figure 14). You will note that among the potential contributions it makes are nutrient (food) materials from treated sewage, brine containing small amounts of petroleum hydrocarbons, trace elements from corrosion protection devices, and other kinds of compounds, as well as a place for plants and animals to attach themselves. The sampling program was designed to determine which of them were present and, if so, their locations and concentrations.

The scientists therefore visited the platform and control stations, as indicated by the sample station map in figure 15. Timbalier Bay had 224 stations, and there were 115 stations offshore as well as along transects or lines drawn from the platform and control sites to shore-based stations, enough to allow gradients to be established if they existed. All field equipment was regularly calibrated against available appropriate standards (both external and internal) to allow comparative correlations to be made from one field trip to the next. Investigators made four, seasonal, 8- to 10-day trips each year for the 2 years. There were many other shorter trips by individual scientists. All of the sampling stations were occupied on each seasonal trip, as well as at other times by either the 23 scientists or some of the more than 30 graduate students involved in the program--many of whom were diving scientists.

The major components of the Gulf of Mexico ecosystem are the phytoplankton, the mainly microscopic floating plants. (See figure 16.) These are the primary producers of the sea; they convert carbon dioxide, minerals, and water to starches and sugars, protoplasm, and other chemical compounds by photosynthesis. They are eaten by the next level in the food web, the zooplankton, which include numerous types of mainly microscopic animals. The nekton are all of those free-swimming animals found in the environment, such as fishes and squid. We will see the importance of bacteria later. The benthos are the bottom dwellers, some attached, some capable of burrowing in the sediments.

Nearly all aspects of the food cycle and ecosystem were studied in the Offshore Ecology Investigation. Certainly, all of the major groups of plants and animals were studied, but not in the same detail. Some of the aspects studied were the total mass and diversity of living material present. This was studied because it seems generally true that the greater the number of different organisms in the environment, the greater ecological health it enjoys and the more stable the environment. The distributions of living plants and animals were carefully measured in terms of where they were found. The results of these investigations showed that there were no differences that could be soley attributed to geographical location except for populations living on platform legs. Because all life forms are sensitive to their environment, the seasonal changes in both temperature and chemical nature were studied in detail. By the end of the study, the project biologists were able to show that these seasonal variations were far more significant than any other variations.

The largest numbers and volumes of samples collected were water samples taken at the surface, at mid-depths and very near bottom to determine oceanographic information such as salinity, temperature, and nutrient and trace element chemistry. Fractions were analyzed for total carbon and organic carbon. For these kinds of analyses, relatively small volumes of water are required; allowing utilization of the Sampling Bottle shown.

Large volume samples were required for the determination of the specific classes of hydrocarbons in the water mass. Therefore, this large volume sampler shown in figure 19 was used to obtain sufficient water to permit the detection and characterization of hydrocarbons.

Plankton nets were towed in order that the mainly microscopic floating plant and animal life could be caught and studied (see figure 20). The scientists needed to know, as a function of carefully measured volume, the nature of the living things floating in the water, their diversity, their effective weight by species, and their hydrocarbon types and amounts. Figure 21 shows a typical concentrated plankton catch, including both plants and animals trapped by the net.

The bottom grab sampler shown in figure 22 takes approximately 1/3 of a cubic yard of sediment each time it is lowered. These sediment samples were required for sediment analysis and to catch the bottom dwelling plants and animals (benthos) living there. The sample is brought back aboard the research vessel where the material is divided and used for study by the biologists and chemists and by geologists determining the nature of the sediments. Some bottom grab samples as well as short sediment cores were collected by divers (see figure 23). Evidences of drill cuttings and muds were sought at all sampling stations but were difficult to differentiate from the normal muds, silts, and sands of the bay and shelf (see figure 24). Where they were identified near a platform by divers, they could not be associated with an adverse impact.

It was mentioned earlier that water samples were taken to allow for the determination of dissolved mineral nutrients (see figure 25). Nutrients enter the living processes in plants and animals and are, therefore, often early affected by materials introduced into the environment. Here, onboard scientists at the sampling station are splitting the water samples for chemical analysis.

Crude oil will float for a while at the surface, forming a filmy sheen. To determine the quantities and fate of these petroleum hydrocarbons, it was necessary to sample the thin floating film. Project scientists developed the sampler shown in figure 26, which would allow them to take a reproducible standard sample and relate the results of chemical analyses to the volume and area that had been sampled. Facing downward is a Teflon disc to which the surface film naturally adhered.

The sampler is lifted aboard the research vessel, where the adsorbed oil and other materials were carefully washed into previously cleaned containers (see figure 27). Scrupulous care is taken to insure that no contamination (such as lubricating oils) gets into the sample during the transfer process. These samples, as well as the large-volume samples, were frozen or otherwise preserved and returned to laboratories--along with samples of fuels and lubricants used aboard the boats--for subsequent comparative studies.

In university laboratories, the biological samples were positively identified, counted, and weighed so that comparisons were possible from place to place on a seasonal basis (see figure 28). Some of the laboratory activities required highly sophisticated and massive equipment, such as the view of a hydrocarbon chemistry laboratory and gas chromatograph and mass spectrometer equipment linked to computers (see figure 29). Such a link makes comparisons possible between samples collected during the project and calibrated standards, and permits identification of separate compounds present. Furthermore, selected animals and some uppermost sediment samples were analyzed to determine their hydrocarbon content.

The typical mass spectrometer tracing in figure 30 shows the hexanesoluble fractions, which are chemical compounds not only found in crude oils but also naturally produced by plants and animals. The peaks in the tracing represent increasingly complex compounds. There have always been petroleum hydrocarbons in this environment due to living processes and natural seeps.

That active oil drilling and production operations do sometimes result in escape of oil to the environment is demonstrated by the infrared image of drilling platforms and the temporary sheen resulting from their activities, shown in figure 31. In the center of the view, a molecule-thick layer of crude oil shows as a lighter blue area stretching between the two rigs. The darker areas that you see below are marsh grasses onshore nearby as they appear on infrared film.

The occurrence of this fresh crude oil on the surface of the water gave the scientists an opportunity to conduct field studies on its behavior and fate. The small floating patch shown in figure 32 was observed for several days.

Twenty-four hours later, the appearance of the oil had changed. Evaporation of some less complex hydrocarbons and microbial and chemical degradation of the oil was relatively advanced. It will be noted in figure 33 that the oil has begun to emulsify and clump.

In order to follow the process and rate of breakdown of the oil under more controlled conditions, experiments were conducted in the laboratory. Flasks were inoculated with both locally produced oil and bacteria found in the area. Here on the left, you note that the bacteria-free oil is still floating on the surface of the seawater with very few globubes and very little clumping. On the right, 24 hours later, bacterial and chemical action has substantially degraded the crude oil; clumping is very far advanced; and much of the material has been converted by bacteria into foodstuffs and byproducts.

In order to better identify and count these bacteria, seawater was placed on suitable materials in shallow plastic dishes using standard microbiological techniques. Here, particularly under the number 14, you see several small, white, glistening colonies of individual kinds of hydrocarbon-degrading bacteria isolated from the study area. These colonies occur in the same numbers in other control areas in the Gulf of Mexico.

As the degradation activities of these bacteria are followed chemically, we go to a microscope view and see large numbers of dark appearing, rod-shaped, living bacteria inside an oil droplet, where they are chemically converting the oil to their own use (see figure 36). An early stage in the conversion is the change of crude oil to fatty compounds identical to those that naturally occur. The fats then enter the food web as an energy source. These experiments indicate that physical and bacterial processes rapidly degrade oil films with the result that there are extremely low amounts of hydrocarbons (average: 5 parts per billion) found in Gulf waters--nor is there evidence of a concentration or buildup of any specific molecule.

One sensitive measure of the gross productivity of the phytoplankton community is the presence and amount of chlorophyll, the green substance in plants that allows conversion of simple compounds into complex food materials. It can be seen in figure 37 that there were significant seasonal changes in chlorophyll content, reflecting the total populations of floating microscopic plants.

Associated with changes in this floating plant community were seasonal changes in the floating animal community, the zooplankton (see figure 38). It can be seen that these seasonal changes follow the seasonal change in chlorophyll. The importance of corroborative studies is clear since, if the seasonal change in zooplankton had not followed the seasonal change in phytoplankton chlorophyll, it would have been necessary to search for other possible explanations of the source of their foods.

The bottom-dwelling community is of great import in the ecosystem. They receive the "rain" of food that sinks down from above. (See figure 39.) Many of the benthos are filter feeders, taking surrounding water through their bodies and digesting out of that water whatever they can. Others eat the muds where they live. It will be noted that the seasonal changes in this community greatly exceeded the differences between a site of man's activity and a control site where there was no such activity. The bottom community offshore from Timbalier Bay is somewhat unusual for the Gulf of Mexico in that a dense layer of very muddy water (the turbid layer) extends for thousands of square miles, effectively preventing light from reaching the bottom. Project geologists traced this turbid layer to its source in the Mississippi River (but it may enter the Gulf through the Atchafalaya River during flood stages) and then laterally along the Continental Shelf. (See figure 40.)

Because the reef effect of platforms is so important, the study of the living things found on their legs deserves further attention. (See figure 41.) Every solid surface is colonized and becomes a reef. Platform legs supported about 6-1/2 pounds of living things per square yard of surface area, more than anywhere else in the study area. (See figure 42.) The net effect of all this growth on platform legs is to increase the available food supply for animals higher in the food chain, since these plant materials are grazed by fish, snails, and other animals which are fed upon, in turn, by the species sought by man.

The simplest of green plants, the algae, who are also near the bottom of the food web, grow on platform legs only in shallower depths where light can penetrate (see figure 43). Where the climatic conditions are favorable, more tropical forms of life will migrate onto the new surface. The white patch (at the bottom) is a tropical coral growing on a platform leg some 15 miles off the Louisiana Coast. It is the first report of this coral growing so far north.

To investigate growth rates, the left side of the leg had been scraped to the bare metal some 45 days before the photograph was made (see figure 44). On the left, it is easily seen that recolonization is rapid. Under clean environmental conditions, it occurs this quickly when a new surface or a recently clean surface is available. On the right, the large white patch is a Bryzoan, a colonial animal form.

In figure 45, barnacles are being overgrown by hydroids (other animal forms). As colonization develops with time, there is both an increase in and a complexity of living things as well as an increasing competition for the available space.

Because the major objective of the entire study was to determine the impact of oil production and drilling on the total environment, beaches separating Timbalier Bay from the adjacent shelf were sampled to see what effects could be measured there. Figure 46, a photograph of oil-saturated sand, was taken on the beach at Timbalier Island. Laboratory analysis of this specific material indicated the hydrocarbon source to be fuel oil, but it demonstrates that oil does get on the beach. Obviously, local concentrations of many hydrocarbons are detrimental to growing organisms; however, the impact of any particular concentration will be determined by how rapidly wave erosion and tidal currents rework the oil into Gulf waters, where bacterial degradation processes are more rapid and effective. (See figure 47.) Field tests here showed that the beach-dwelling animal communities were not harmed.

From the fish-catch, shrimp-catch, and oyster-harvest data shown plotted here with oil production through the years in this region of Louisiana, it can be seen that these catches of commercial importance have not decreased as oil production has increased; indeed they have increased! This is not to say that increase in catch is a result of industrial activity; however, it is still found that catches have not suffered while oil drilling and production have increased greatly during the same years.

The deceptively simple question asked in the beginning of the project did not turn out to have a simple answer.

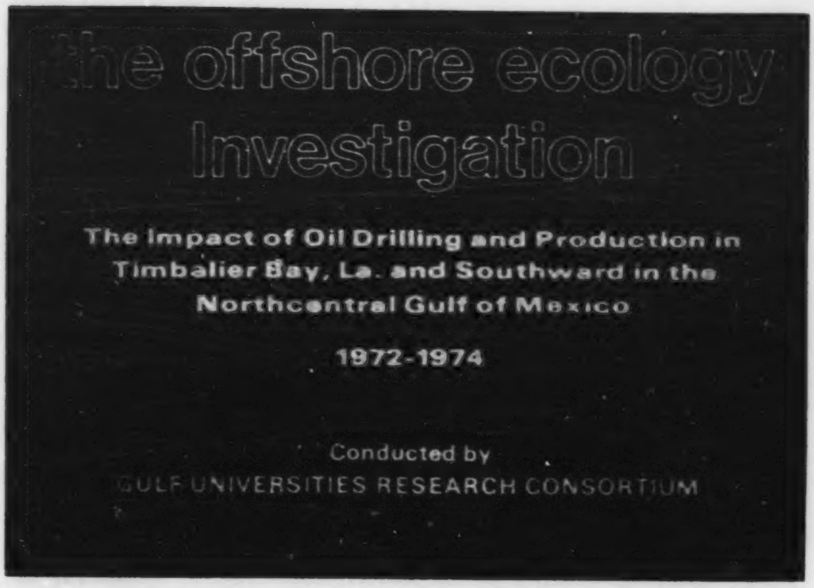
Based upon the data analyses thus far, several general conclusions can be reached from this comprehensive Offshore Ecology Investigation:

1. It questions the universal necessity for conducting a "before-the-fact" baseline study to subsequently determine the environmental impact of this type of man's activity.
2. Natural phenomena such as seasonality, floods, upwellings, and turbid layers have much greater impact upon the ecosystem than do petroleum drilling and production activities.
3. Concentrations of all compounds of OEI interest that are in any way related to drilling or production are sufficiently low to present no known persistent biological hazards.
4. Every indication of good ecological health is present. The region

of the sampling sites is a highly productive one from the biological standpoint, more so than other regions thus far studied in the Eastern and open Gulf of Mexico.

5. Timbalier Bay has not undergone significant ecological change as a result of petroleum drilling and production since just prior to 1952, when other, more limited, baseline data were generated.

FIGURES



the offshore ecology
Investigation

The Impact of Oil Drilling and Production in
Timbalier Bay, La. and Southward in the
Northcentral Gulf of Mexico

1972-1974

Conducted by
GULF UNIVERSITIES RESEARCH CONSORTIUM

Figure 1.

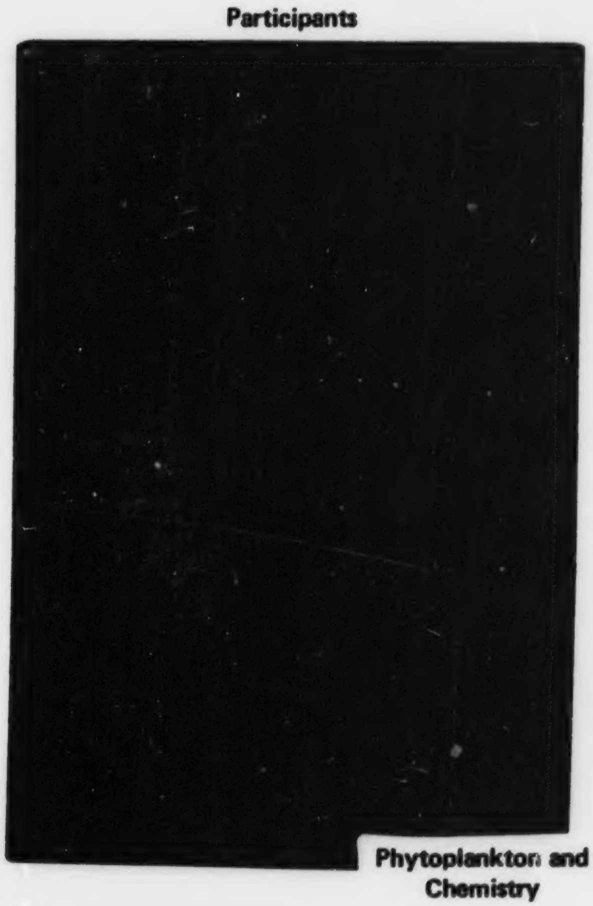

Participants
Phytoplankton and Chemistry

Figure 2.

Participants con.

Figure 3.

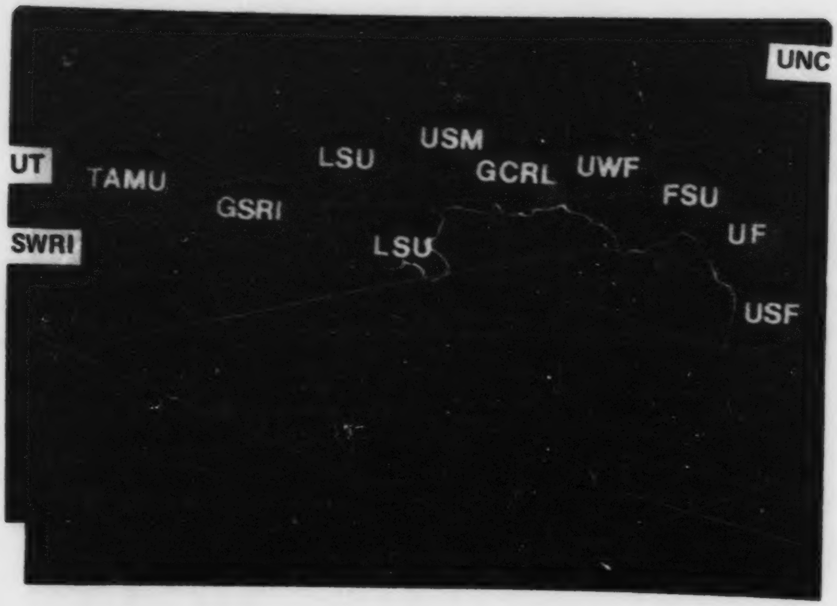

UNC
USM
UT
LSU
GCRL
UWF
TAMU
FSU
GSRI
SWRI
LSU
UF
USF

Figure 4.

Figure 5.

Figure 6.

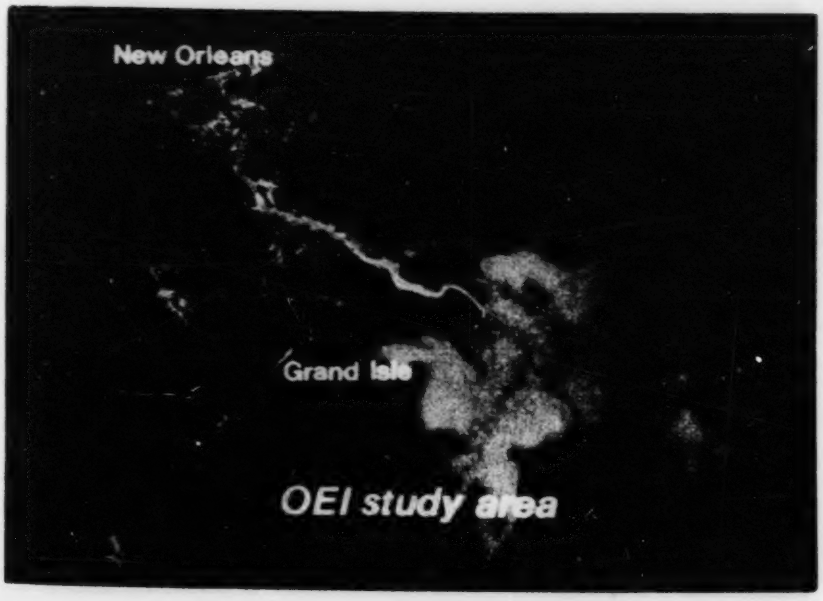
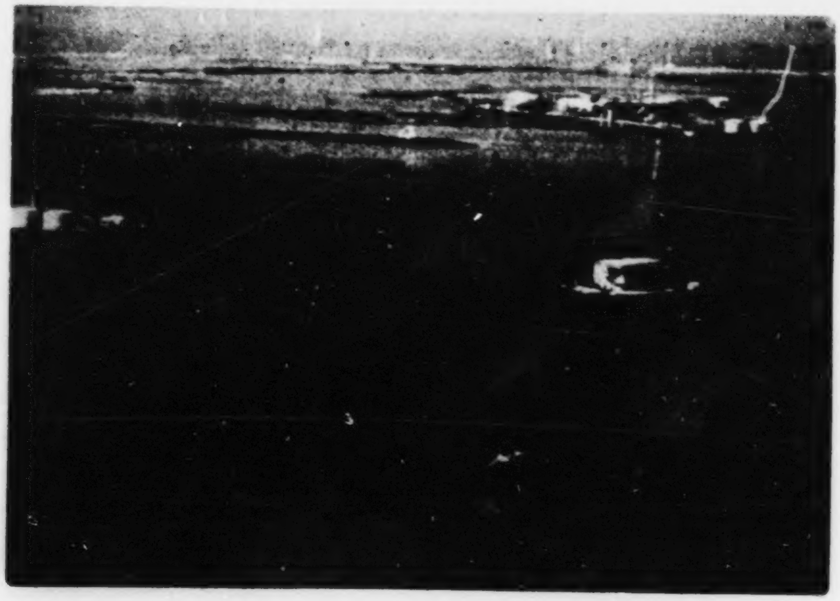

New Orleans
Grand Isle
OEI study area

Figure 7.

THE BAY,
BEACH, & SHELF

Figure 8.



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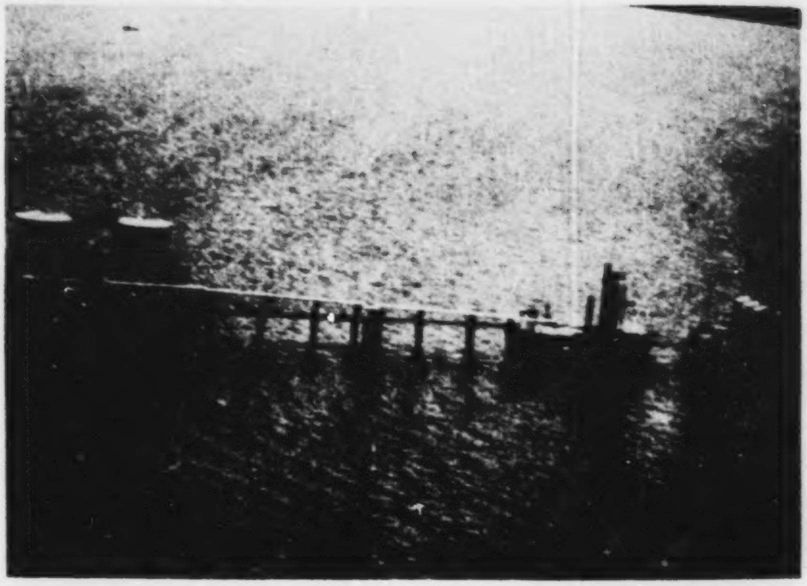
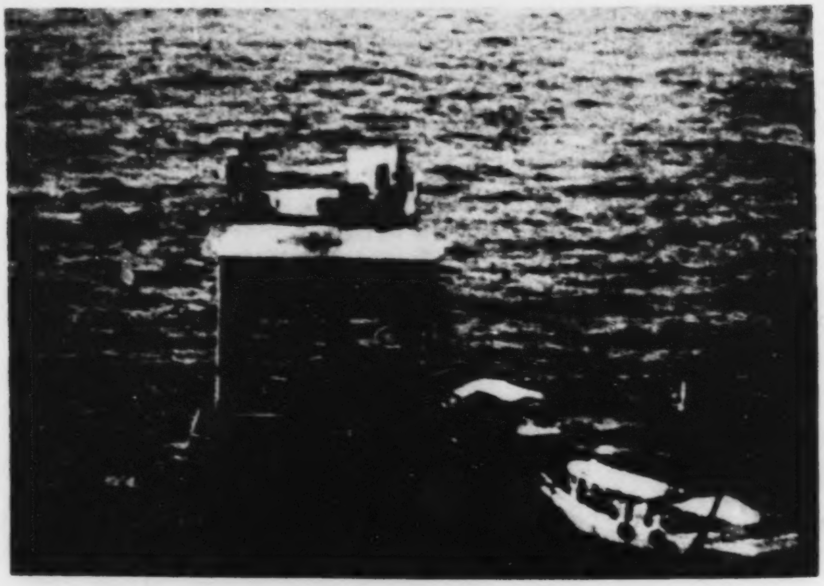


Figure 10.

Figure 11.



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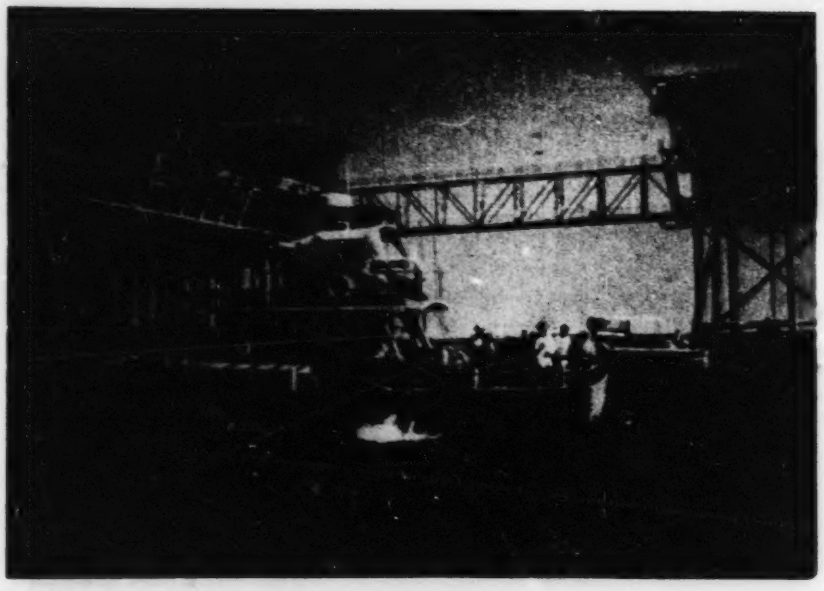


Figure 13.

PHYSICAL/CHEMICAL RELATIONSHIPS

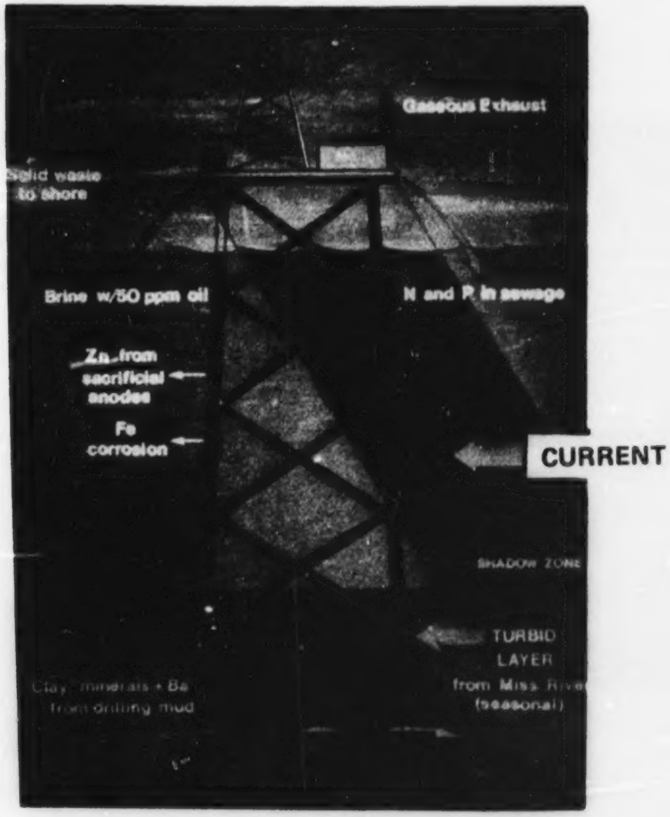

Gaseous Exhaust
Solid waste to shore
Brine w/50 ppm oil
N and P in sewage
Zn from sacrificial anodes
Fe corrosion
CURRENT
SHADOW ZONE
TURBID LAYER from Miss River (seasonal)
Clay minerals + Ba from drilling mud

Figure 14.

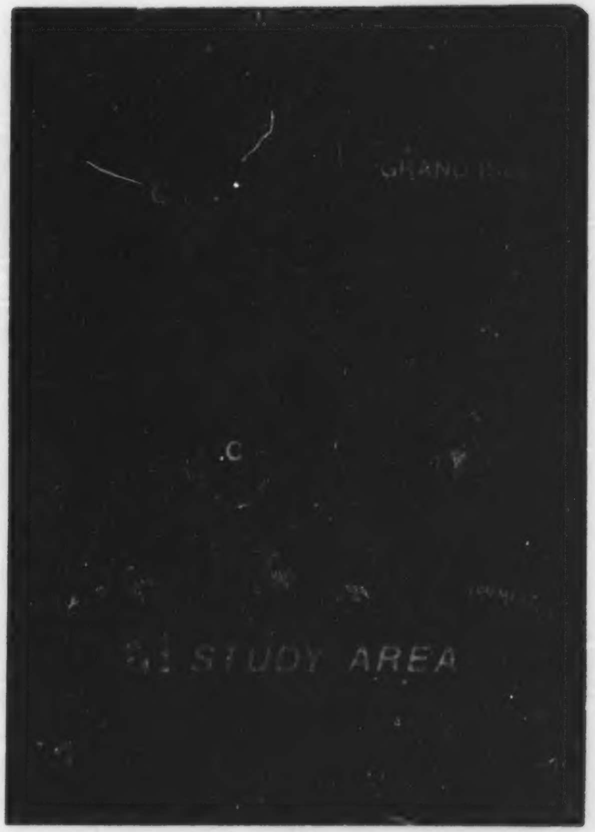
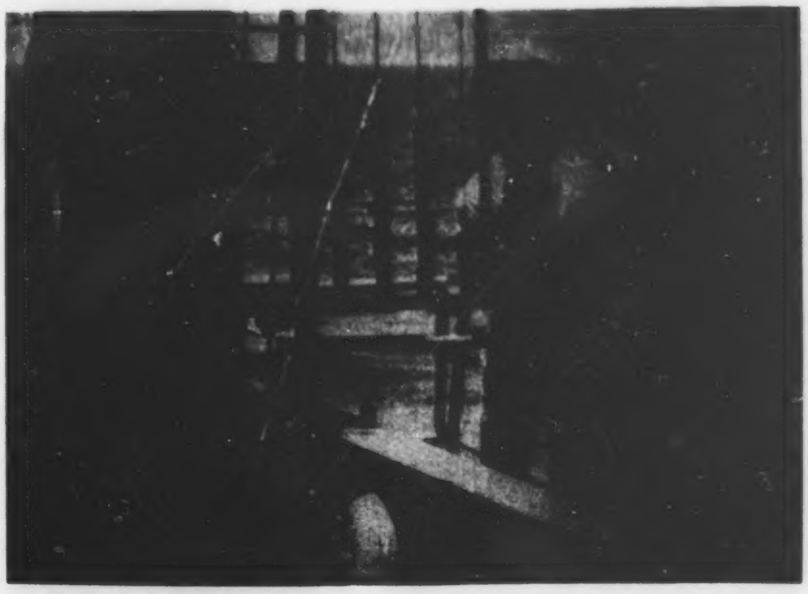

GRAND
STUDY AREA

Figure 15.

PHYTOPLANKTON
ZOOPLANKTON
NEKTON

Figure 16.

Figure 17.



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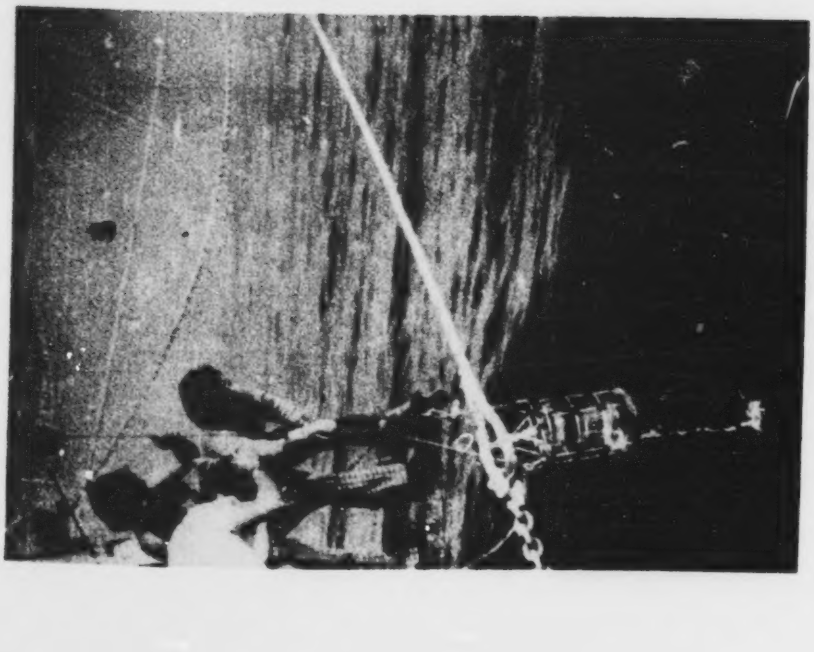
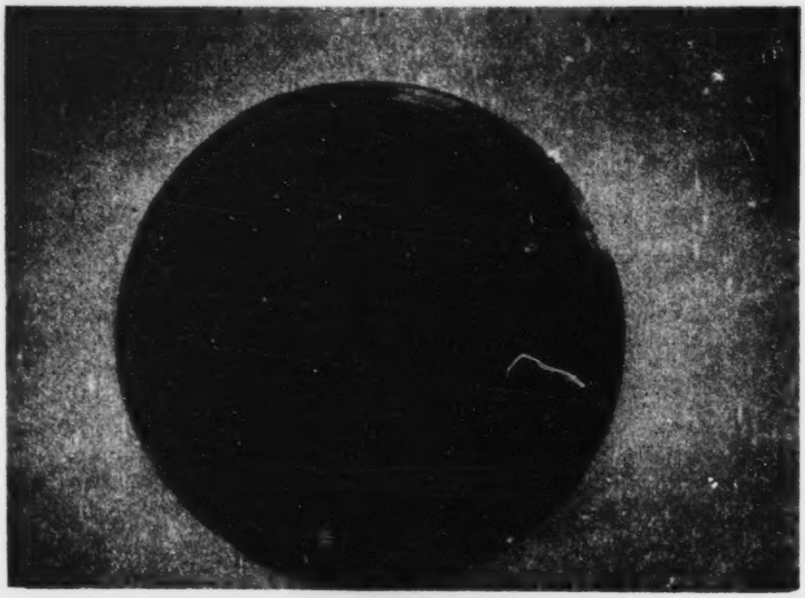


Figure 19.

Figure 20.



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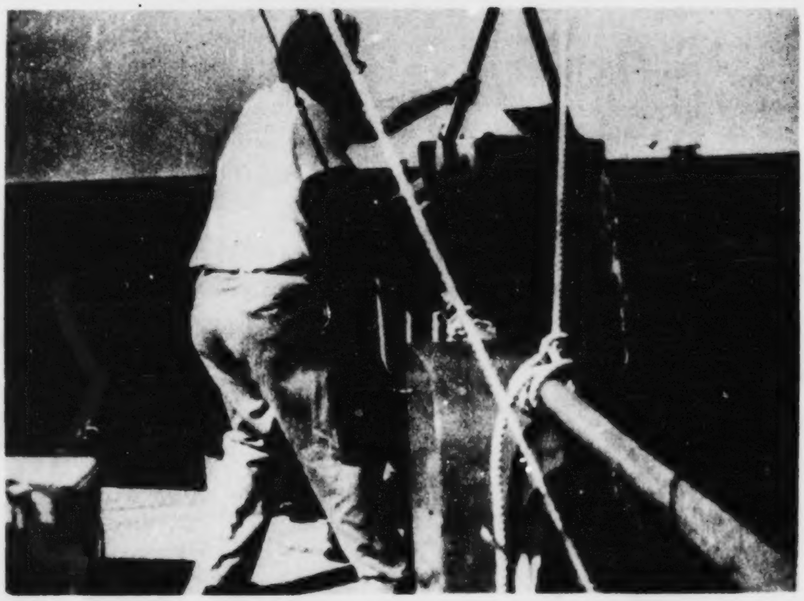
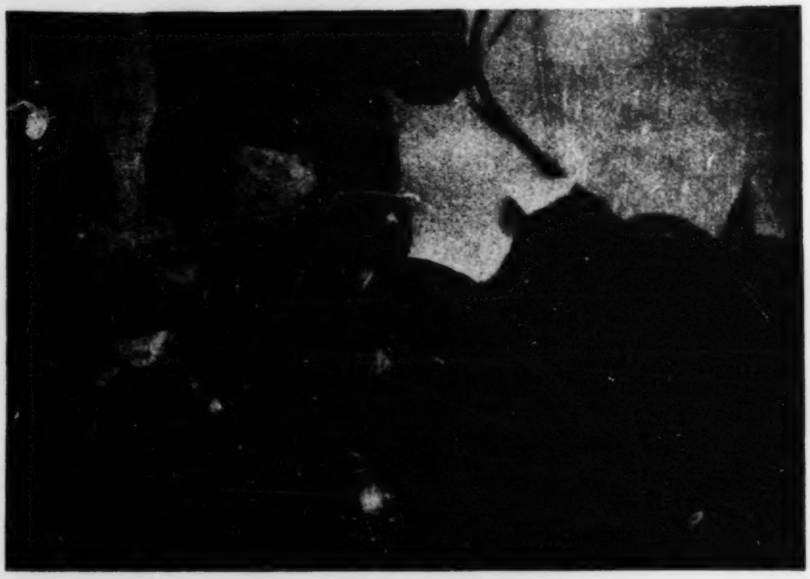


Figure 22.

Figure 23.

Figure 24.



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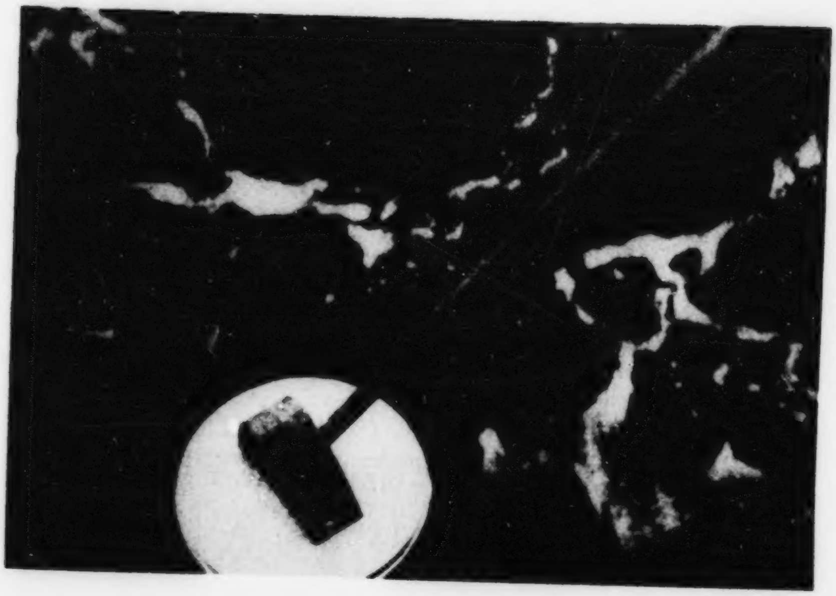

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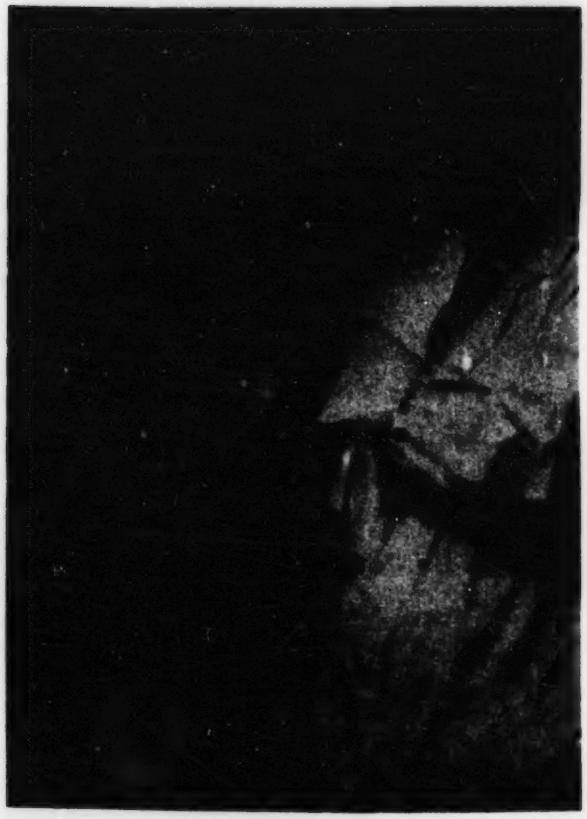
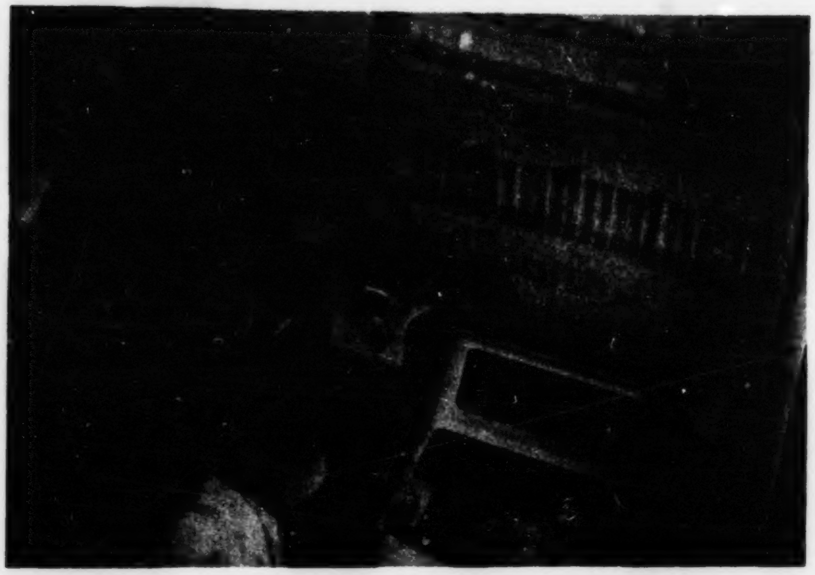


Figure 27.



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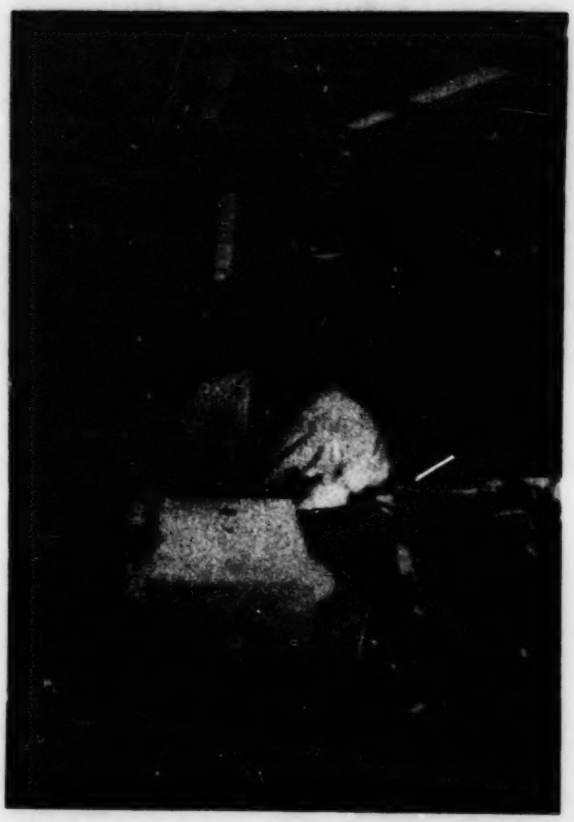

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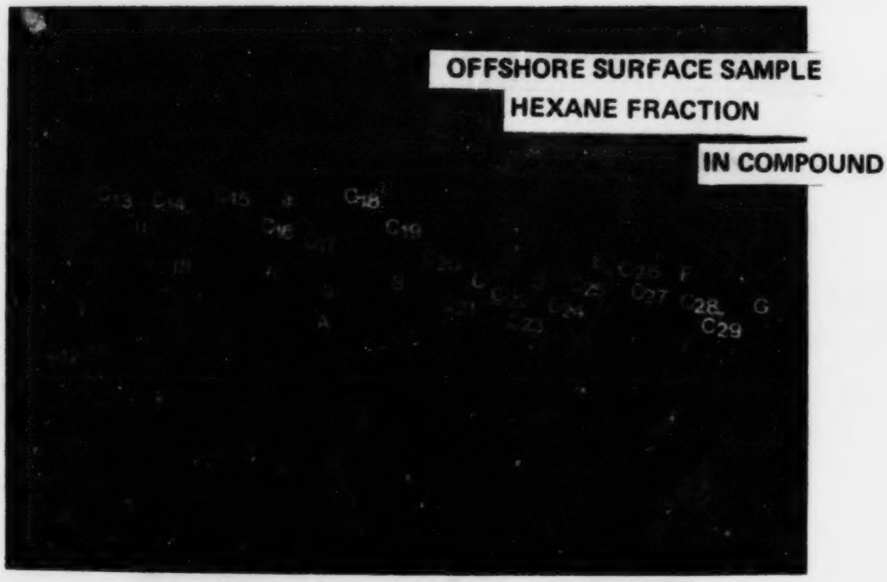
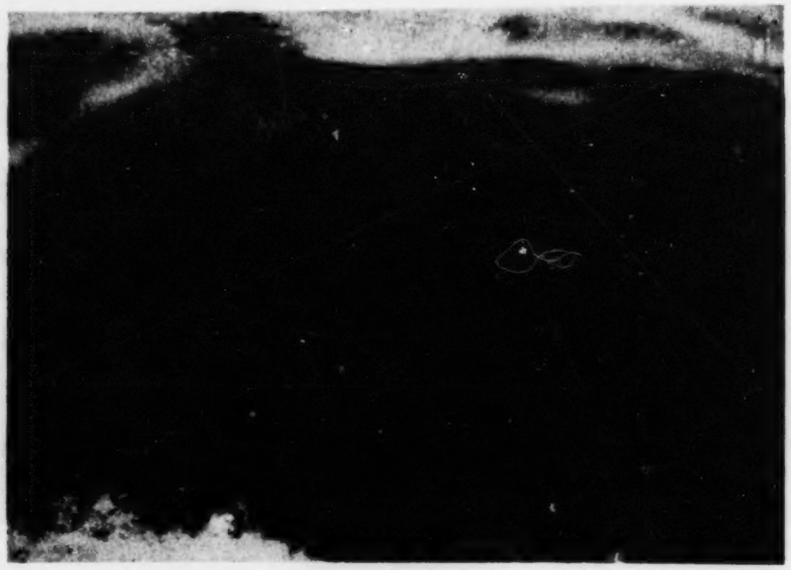


Figure 30.

Figure 31.



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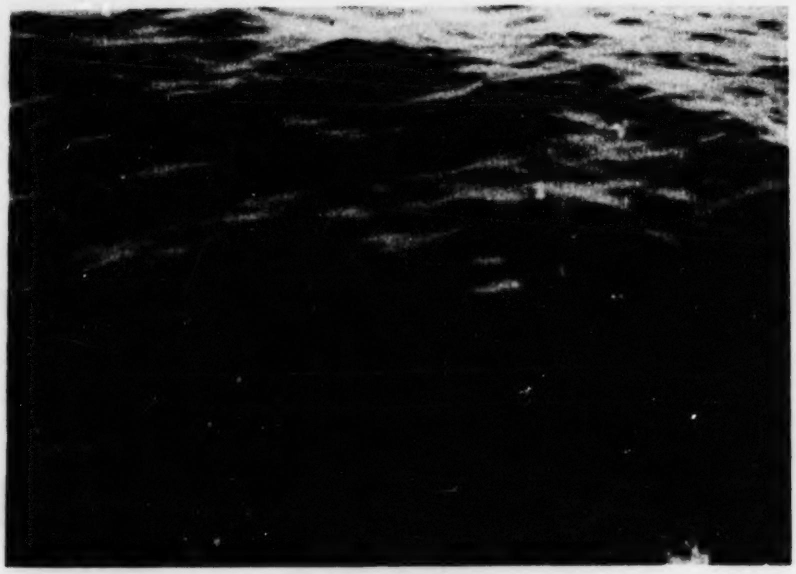

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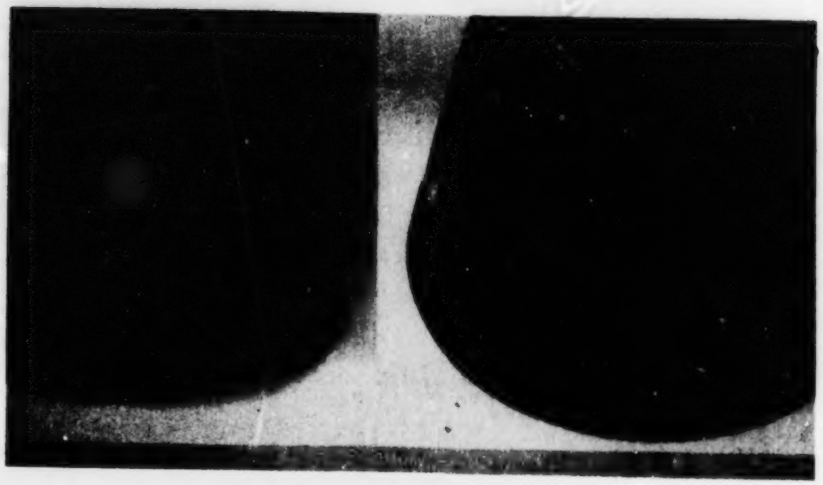

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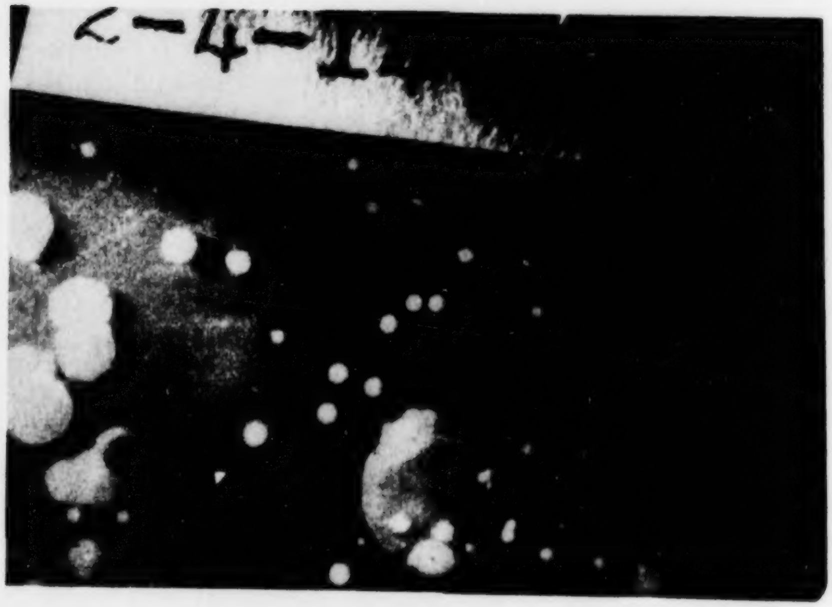

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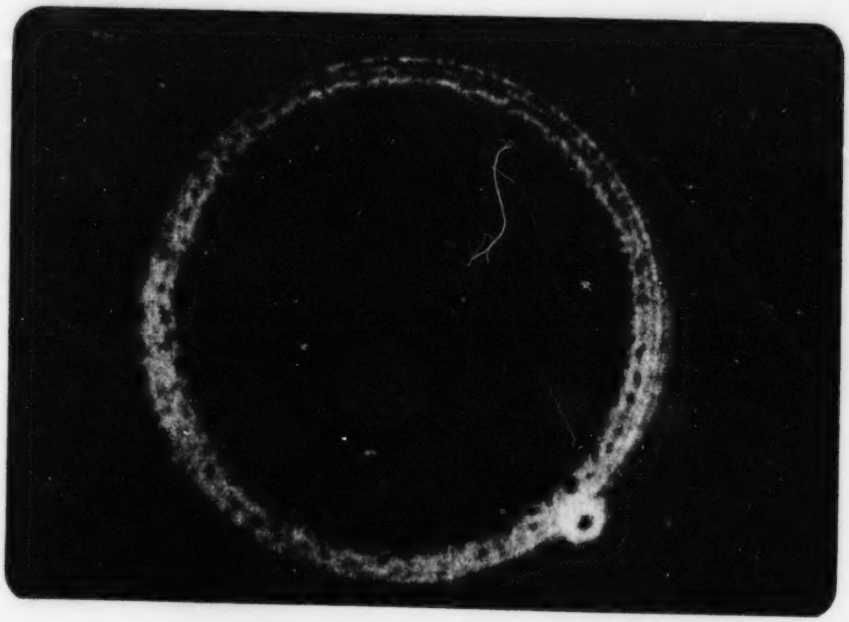

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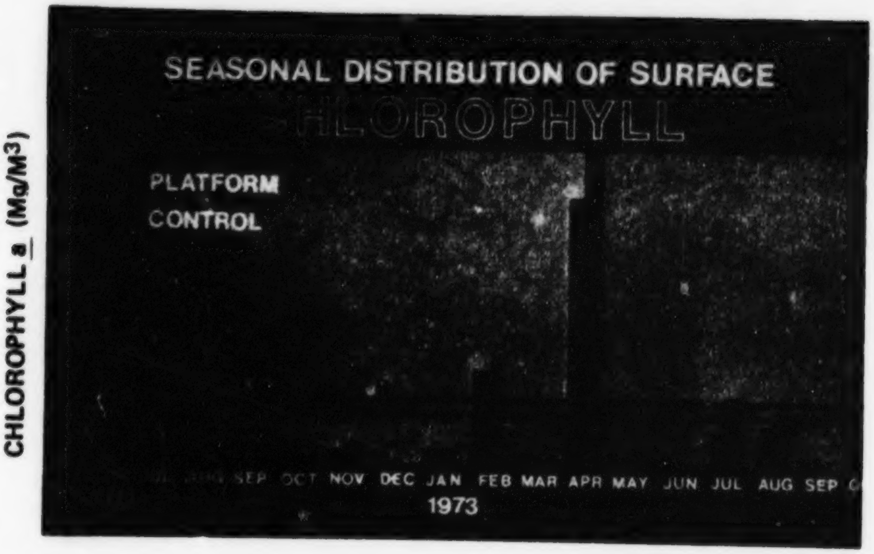

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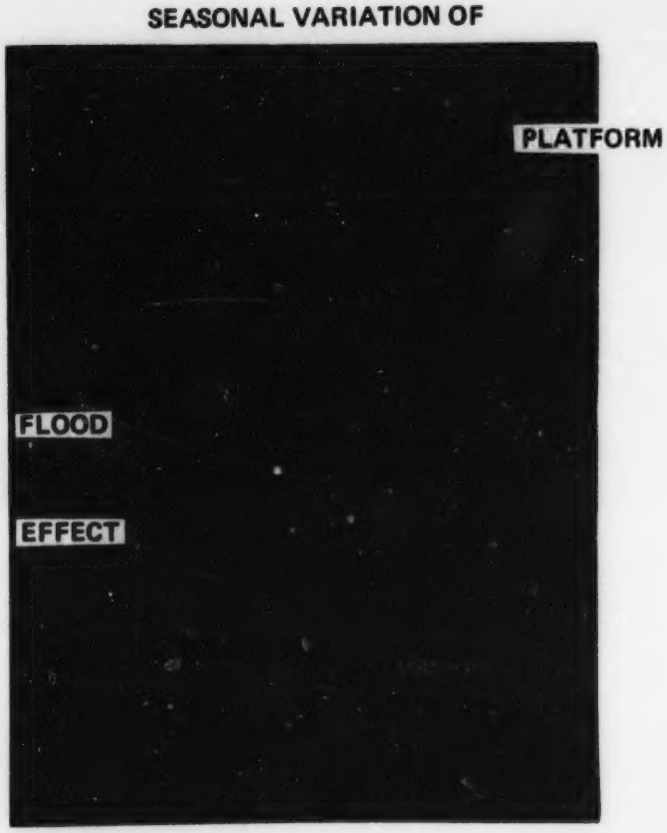

SEASONAL VARIATION OF
PLATFORM
FLOOD
EFFECT

Figure 38.

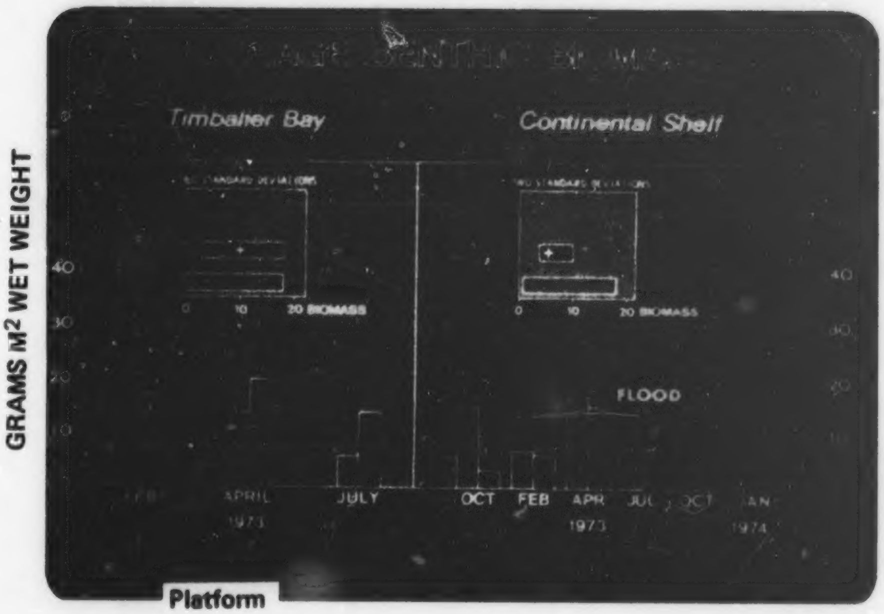
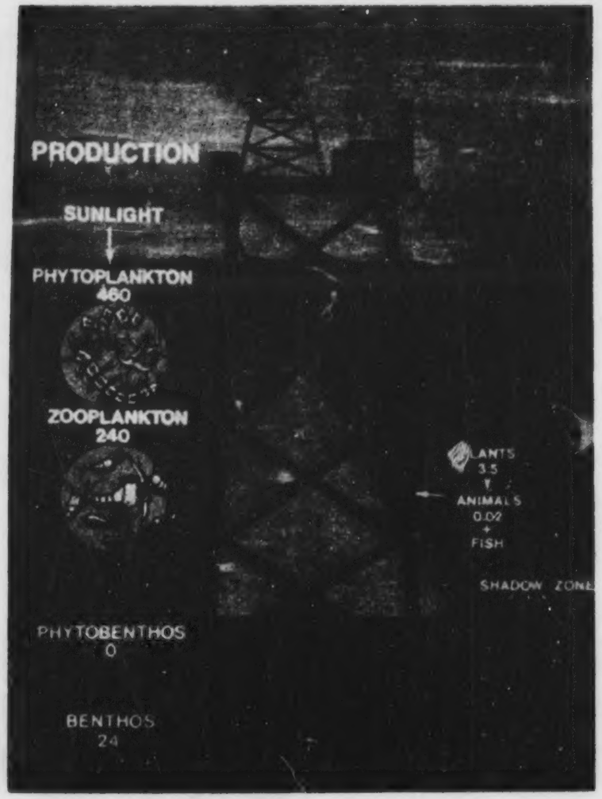

GRAMS M2 WET WEIGHT
Timbalier Bay
Continental Shelf
TWO STANDARD DEVIATIONS
0
10
20 BIOMASS
40
30
20
10
FLOOD
APRIL
JULY
1973
OCT
FEB
APR
JUL
OCT
JAN
1973
1974
Platform

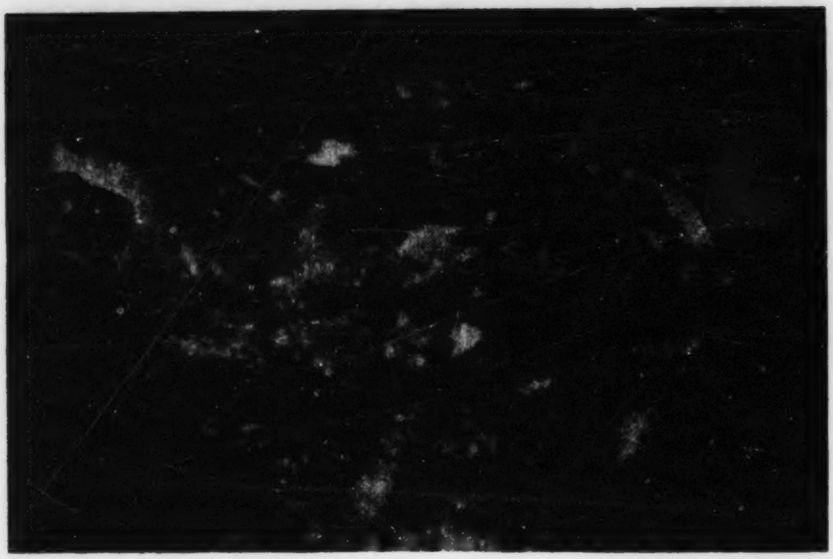
Figure 39.

Figure 40.



PRODUCTION
SUNLIGHT
PHYTOPLANKTON
460
ZOOPLANKTON
240
PHYTOBENTHOS
0
BENTHOS
24
LANTS
3.5
ANIMALS
0.02
FISH
SHADOW ZONE

Figure 41.



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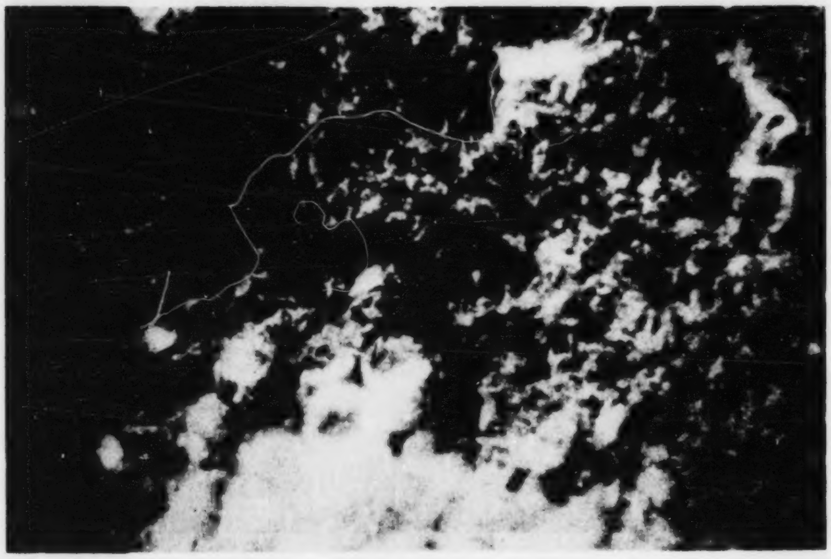

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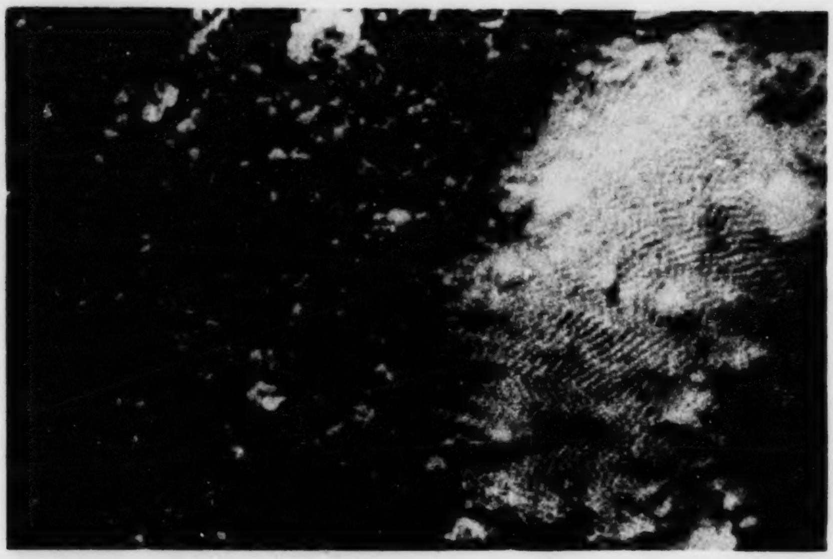

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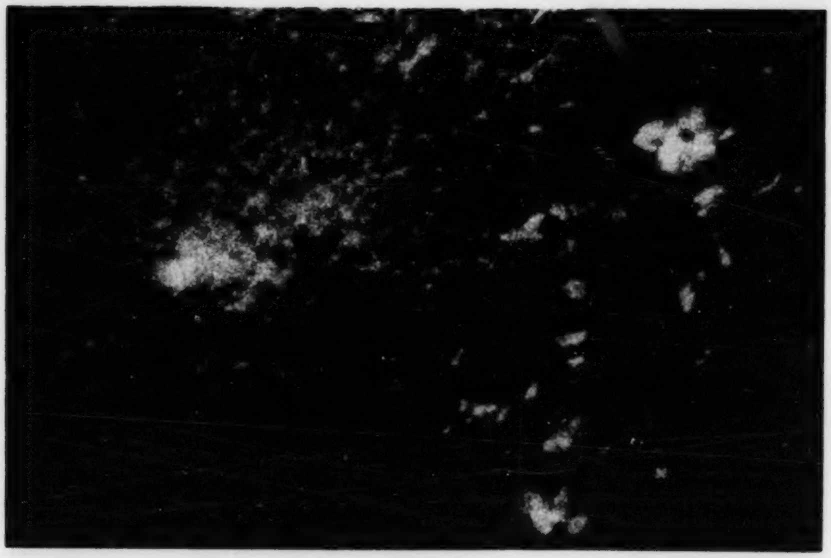

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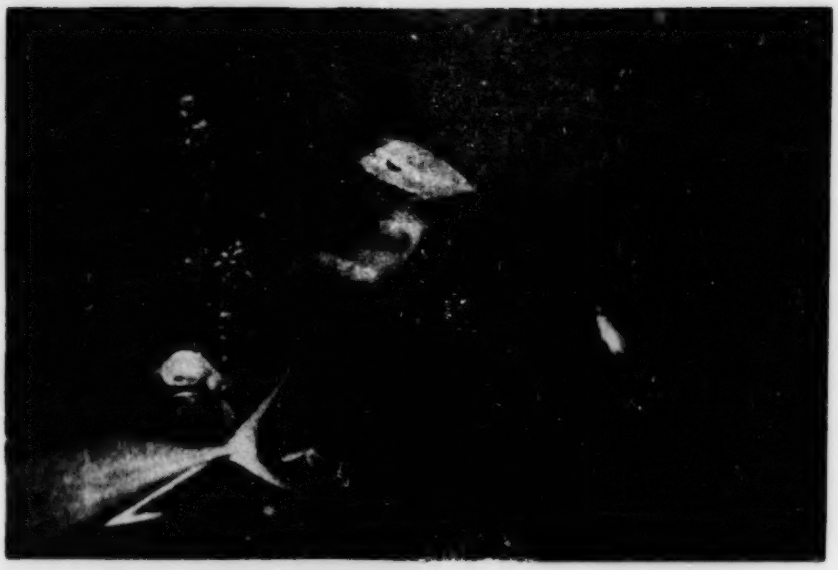

Figure 46.

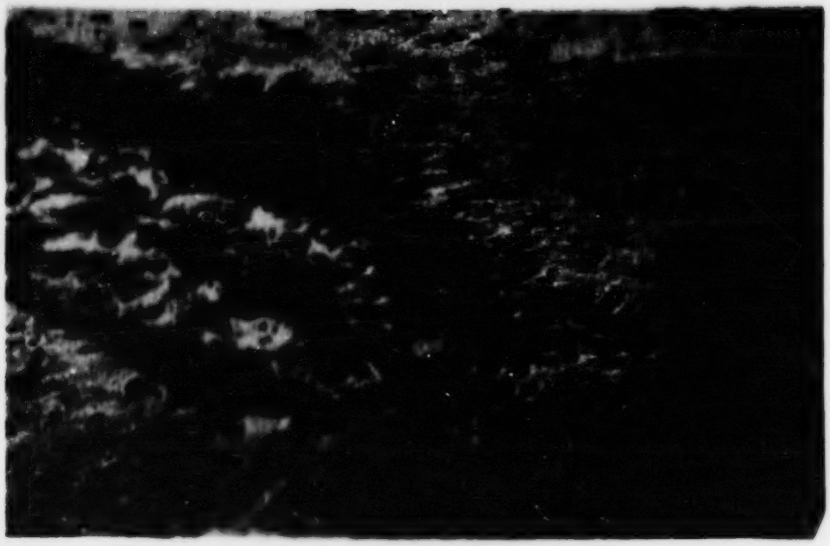

Figure 47.

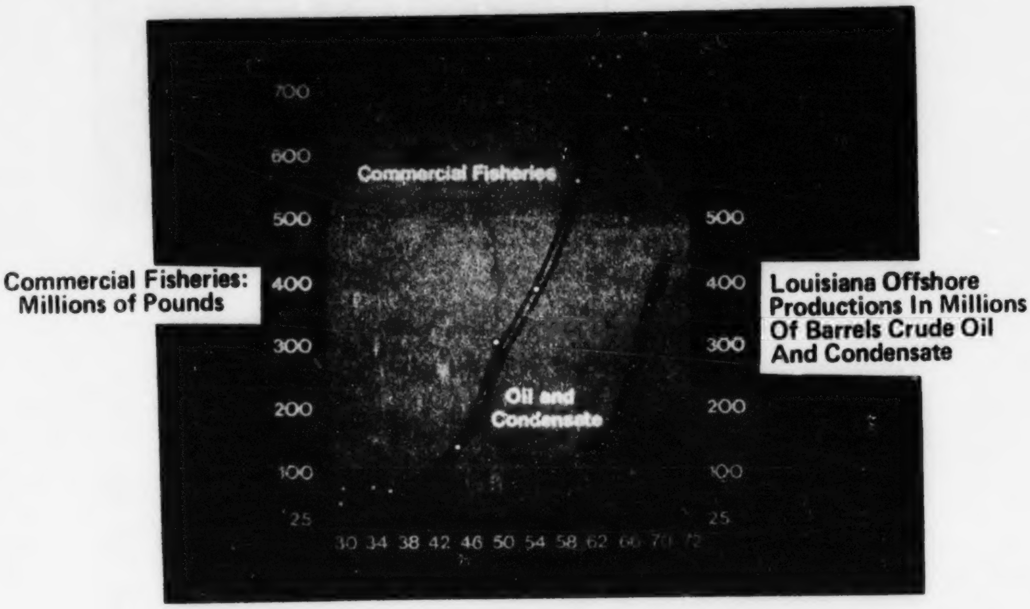
700
600
Commercial Fisheries
500
500
Commercial Fisheries: Millions of Pounds
400
400
Louisiana Offshore Productions In Millions Of Barrels Crude Oil And Condensate
300
300
Oil and Condensate
200
200
100
100
25
25
30 34 38 42 46 50 54 58 62 66 70 72

Figure 48.

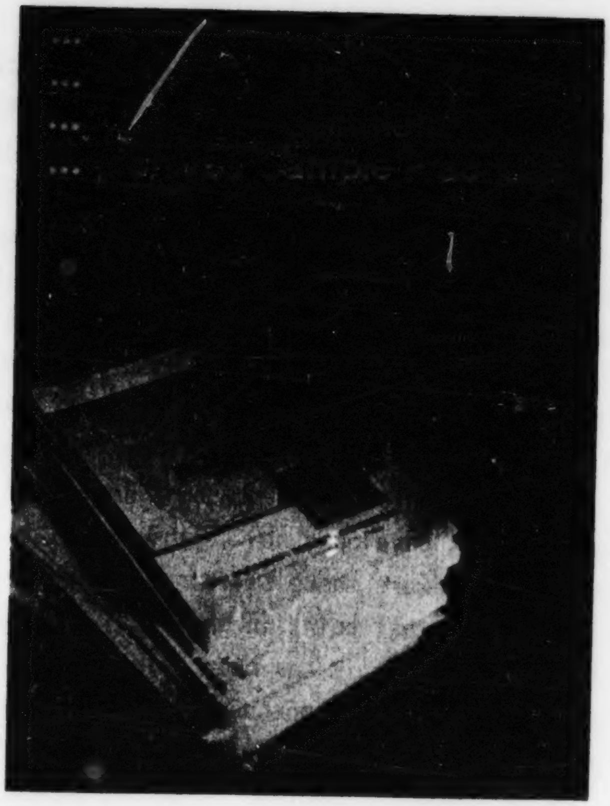

Figure 49.

DISCUSSION

MR. DONALD MOORE (National Marine Fishery Service, Galveston, Texas): Mr. Tyson, I want to make some observations on what is shown in one of your graphs.

One of the major components of the commercial fishery in Louisana today--the poundage which I believe your graph included--is the menhaden fishery, which primarily did not exist at the time when the commercial catches on your graph started. The menhaden fishery developed as the commercial market developed; the resource was there all the time. It was a case of the economic and technical situation becoming such that a new fishery was developed.

What I am leading to is that this dramatic increase does not show that the oil development had an impact; neither does it indicate that it did not have an impact on the resources available. It is just that the fishery, through the economic incentives and the technical development, developed new capabilities, to tap additional fishery resources that were there all along during that period.

MR. TYSON: I tried to make that point in the text, that the two were not necessarily associated; it has been said by some that fewer fish are being caught but the total poundage just does not indicate that at all. More fish are being caught today than have ever been caught before, for all the reasons you have named and others.

MR. PAT M. WENNEKENS (Alaska Department of Fish & Game, Anchorage, Alaska): I am a little puzzled about some of the conclusions you arrived at. This has not shown that damage has been done or not been done.

You go back to what year--1934, 1937?

MR. TYSON: The first well was drilled in Timbalier Bay in 1937.

MR. WENNEKENS: But the question is, what is baseline? What do you compare against, in terms of the basic environment? Do you compare with what you have now, more or less?

MR. TYSON: In our case, we are comparing controlled areas, which are adjacent to our study sites: so therefore you are within the same physical variable regime and have the same ecosystem but have never experienced any drilling or production activity.

MR. WENNEKENS: No, I am not saying what the base line was before you had a lot of human impact on the area.

MR. TYSON: A base line did not exist before.

MR. WENNEKENS: Okay. So, just for the sake of argument--

MR. TYSON: Let me continue this just a little bit further where a base line does exist, which is prior to our study. For example, the 1952 study that I mentioned dealt primarily with the crustacean populations in Timbalier Bay. And so you are looking at over a 20-year period without seeing any change in those populations.

MR. WENNEKENS: Well, for the sake of argument, I just have to draw some kind of a parallel to the situation.

Let us say that you are dealing with an environment which has been essentially in use for a long time, and to assess a given level of impact, you make a study and find out that a number of primary forms of life, such as various plants, are quite abundant, that you also have a certain abundance and diversity of insects, that certain species of birds are also very abundant in the area, and that several different types of mammals are actively feeding. However, what I describe are the conditions for a garbage dump, which is a very productive type of environment. And the question is, unless you have something to compare before such a condition develops, what do you have in the area, prior to large impact, to compare against in terms of the baseline environment?

What you might have right now is a condition in which you have a population that is adapted to pollution; and you are trying to measure pollution effect on pollution-resistant forms.

MR. TYSON: Thank you. I do not have any reply.

MR. DENNIS G. WRIGHT (Environment Canada, Winnipeg, Manitoba, Canada): Although the crustacean population has increased in Timbalier Bay in the last--

MR. TYSON: I did not say it had increased. I said it had not changed.

MR. WRIGHT: Had not changed. Has not the species composition shifted somewhat?

MR. TYSON: No.

MR. WRIGHT: Has not there been a change from, say, the white shrimp to the brown shrimp?

MR. TYSON: No. That part of the crustacean population is not the part I am talking about. The part that I am talking about has not been changed at all.

MR. WRIGHT: I see. Your graph on the benthos shows an extreme seasonal cycling. What was the one axis on your graph showing? The weight of the organisms, or the quantities, or what?

MR. TYSON: It was biomas.

MR. WRIGHT: Did you subject that data to any information analysis, species diversity, or other?

MR. TYSON: Yes.

MR. WRIGHT: Was there any change there?

MR. TYSON: No, no significant change.

MR. CHARLES F. JELINEK (Food & Drug Administration, Washington, D.C.): In the analyses you carried out, did you analyze for heavy metals at all or for any identified organic chemicals?

MR. TYSON: We did look for the so-called heavy metals. We did not look for the so-called pesticide types of compounds.

MR. JELINEK: Do you remember which metals you did analyze for among the heavy ones, like mercury, lead, or so on?

MR. TYSON: Would you care to speak to that, Dr. Montalvo?

DR. MONTALVO: We looked at the heavy elements in the water column later on and not in biota or sediments. That is the first point I want to make.

Secondly, the heavy metals that were looked at in the water column were lead, mercury, cadmium, zinc, and I think arsenic; five of them. As we went further away from the rig, we found a decrease in concentration of lead, cadmium, and zinc. However, the differences between the concentration of metals at the rig and at the control samples, I think, was in the same order of magnitude as the seasonal variations of the metals that were obtained.

MR. TYSON: In addition to the analyses that Dr. Montalvo conducted, there were some 13 other elements for which analyses were made.

MR. JELINEK: But did you carry them out on any living organisms?

MR. TYSON: Yes, they were carried out on some of the body tissues by another investigator for some of the elements, zinc particularly.

MR. GEORGE H. HOLLIDAY (Shell Oil Company, Houston, Texas): Would you classify Timbalier Bay as a wasteland or a garbage dump now?

MR. TYSON: One can go to Timbalier Bay any time of the day or night and find sports fishermen and commercial fishermen working the bay. If you fly over the area, as we have done, you can see a motorboat at the end of a plume of mud that it has stirred up. When you fly back over it 7 or 8 hours later, you can still see that plume of mud that has been stirred up.

It is not a wasteland, at all. In fact, some of you may be from Cajun country, and would get the Chamber of Commerce pitch pretty quickly, I suspect.

MR. WRIGHT: Sir, have you been able to identify any layers of bentonite on the bottom around drilling sites.

MR. TYSON: We have not been able to identify any layers of bentonite.

What you are dealing with is a kind of material that is dumped into that part of the Gulf of Mexico in such quantities that man's addition to it--assuming the largest size borehole in the deepest well, over a period of 45 years, and making some simple arithmetic calculations--will give you a layer something like an eighth of an inch thick if it were uniformly distributed. You cannot find any heaps or piles of it; it is dispersed very rapidly.

MR. WRIGHT: A lot of clay materials have been dumped in. What is the primary type of clay that is flowing into the area?

MR. TYSON: It is a bentonite.

MR. WRIGHT: Bentonite or montmorillonite?

MR. TYSON: It has large percentages of the montmorillonite also. You see, it comes from places like St. Louis and northward.

MR. WRIGHT: I see. It has been my experience--working in the lakes in Northern Canada--that we have examined a couple of lakes where bentonite has been spilled as a result of a breach in a drilling sump, and we have been able to see accumulations of bentonite on the bottom. In these areas, the bottom fauna has been severely reduced.

MR. TYSON: I can see where in a lake one might easily see that. As you know, bentonite is often used by lake owners to seal the bottom.

MR. WRIGHT: Right.

MR. DONALD MOORE: I want to make an observation that I made at another conference where you gave this paper, since we have brought up the condition of the Timbalier Bay and the environs. One aspect you did not go into in your study was the lacing of the marsh with access channels, pipeline channels, etc. A recent examination of sequences of aerial photos has shown that the marsh deterioration in those areas is much accelerated to other areas.

MR. TYSON: This certainly has happened. One other thing, in all fairness, should be said about Timbalier Bay: its bottom is nearly paved with iron pipe, so it is very difficult to use a magnetic compass in the area.

MR. GORDON W. LAWSON (Swaco, Houston, Texas): I would like to ask our fishery friends here if they have any data going back to the World War II period when so many tankers were sunk off the Gulf and Atlantic coasts to indicate how this affected the fishery and what not, and how long it took the fishery to recover. Have you all studied that?

MR. MOORE: I do not believe the data during that period was all that good. I am just speculating now, but our sampling agents were probably somewhat decimated by the conscription at the time. Also, with the shrimp for instance, our excellent sampling data has only been occurring since 1962, when we started to collect the detailed shrimp statistics. We had more generalized statistics prior to that; what the quality was back in the forties, I would not care to speculate.

CHAIRMAN GIAM: Joe, who funded this project of yours?

MR. TYSON: The program was funded by 82 corporations, which included the offshore operators, the service companies, banks, private foundations, the universities. In some cases even the principal investigators funded a part of their activity, but the funds came from a very diverse source. The stipulation placed on the program by our board of trustees, and by the sponsors, was that all of the data would be freely published and available to all who desired it, immediately, but that there would be no special reports. I am happy to say that there have been none.

MR. MICHAEL J. HARDIN (Environment Canada, Yellowknife, N.W. Territory, Canada): Mr. Tyson, even though your activities were restricted to Timbalier Bay, it is likely that people will try to extrapolate them to other areas where offshore drilling is either contemplated or will be increased. Now, the ecosystems that you studied were highly productive and diverse, and therefore were likely to be more resistant to disruption and change.

However, I am wondering if you would like to speculate on whether or not less productive ecosystems could adapt equally well to the sort of impacts that you have observed in Timbalier Bay?

MR. TYSON: I am unwilling to speculate, as you might surmise.

However, we are just completing a series of data collection exercises in the Laguna de Terminos in the Bay of Campeche which has, thus far, throughout its history, experienced only native agricultural practice. And it is a less diverse environment.

So we will see how much extension we can make of this OEI data to that kind of a situation.

Now, admittedly, the temperature regime and the seasonality are very similar in those two locations.

When you go to an environment in which the temperature ranges are much greater, and in which the biota have already responded to substantial physical stress or environmental stress, then it remains to be seen how resilient they will be. But to live in certain parts of the Arctic or the Antarctic zones takes a mighty flexible organism.

EFFECTS OF DRILLING OPERATIONS ON THE MARINE ENVIRONMENT

R. P. Zingula*

Abstract

Studies by Exxon scientists and others show that offshore drilling operations are not as harmful to the marine environment as some people have either proposed or feared. In the Louisiana offshore and many other areas, rivers contribute so much sediment that any resulting from drilling is negligible. Water samples taken while drilling show a very rapid drop, to a low level, of suspended solids in a short distance downstream from the rig.

Cuttings accumulating on the sea bottom do not create deserts. Studies made using scuba show that mobile organisms are active on the surface of the pile even while drilling is going on; and in a few months' time these organisms turn it into "normal" sea bottom.

Analyses have been made of seawater samples downstream from drilling operations. The common chemicals normally used in drilling--caustic, barite, chrome lignosulfonate, etc.--are present in such small quantities that chemical interaction and dilution make their effect negligible.

Introduction

A number of people have expressed concern over the possiblity that cuttings and drilling fluids released into the water during offshore drilling operations are harmful to the marine environment. Specifically, they have been concerned with (1) solid drill cuttings, (2) finely divided particles or mud, and (3) drilling mud additives. It has even been suggested that such operations leave behind permanent graveyards. Studies by scientists from Gulf Universities Research Consortium, and by Exxon, Shell, and scuba divers from other sources have reinforced the conclusions reached by other investigators that the effects of these discharges are both negligible and short-lived.

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*Senior Professional Geologist, Exxon Company, USA, Houston, Texas 77001.

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diver surveys and side scan sonar records that we have seen have shown accumulations in the Gulf of Mexico to typically be approximately 150 feet in diameter, with the outline being circular, elongate, or star burst, depending on currents (figure 1). Maximum elevation of these piles immediately after drilling a well appears to be less than 3 feet, thinning rapidly toward the edges. Side-scan records of wellsites in the Gulf of Mexico and Santa Barbara Channel several months after drilling has been completed present no definite "shadows," thus indicating that the height of the cuttings pile is less than 6 inches. This means that some combination of compaction, redistribution by currents, settling into the bottom, and disaggregation of the chips destroys the pile fairly rapidly.

Mobile benthic and planktonic and nektonic organisms are little affected by the drilling operations and the accumulation of cuttings on the bottom. It should be remembered that cuttings drift down as individual small chips and not as a solid blanket. In October 1971 a team of Exxon (then Humble) scuba diving geologists and paleontologists studied and photographed the cuttings accumulating under a rig that was currently drilling. The jack-up rig Dixielyn 10 was at the time drilling in 80 feet of water in South Timbalier Block 111 (figure 2). The rig had been drilling for 14 days and at that time had reached a well depth of 11,000 feet. During the time the rig had been on location, the current had been mainly in one direction, and the cuttings pile was well delineated on the upstream side.

The diving team followed the cuttings from where they first hit the water at the downpipe to where they came to rest on the sea bottom. A number of individual fish swam through the area of descending cuttings, and during the time the divers were in the water several schools of moonfish or lookdowns were seen to pass through the area of cuttings and muddy water. None of these fish showed any signs of distress from either the cuttings or the associated mud. Indeed, several times spadefish took individual cuttings into their mouths thinking they were food, only to spit them out with no sign of distress after finding that they were not edible.

Drill Cuttings

There is no question that the accumulation of cuttings under the downpipe will be harmful or possibly lethal to many of the sessile benthic organisms in that small area. The amount of biologic damage is dependent upon the areal extent and thickness of accumulation of cuttings, which is in turn dependent on many factors such as the depth of the well; hole size; type, thickness and hardness of sediments penetrated; strength; duration, and direction of the various currents; water depth; storm action; depth of bottom of downspout; etc. There is no hard and fast rule as to what the shape, thickness or extent of accumulation will be. However,

Figure 1. Side-scan sonar shadogram of cuttings accumulation on the sea bottom of a typical Gulf of Mexico well. The dark starburst pattern is the areal extent of the cuttings, which are denser than the surrounding sediments. Maximum extent of cuttings is 50 meters from the borehole. Lack of strong shadows from the cuttings indicates that there is no high relief on the accumulation. The light area in the center of the starburst is the shadow caused by the depression left when the casing was cut off below the mudline and pulled out.

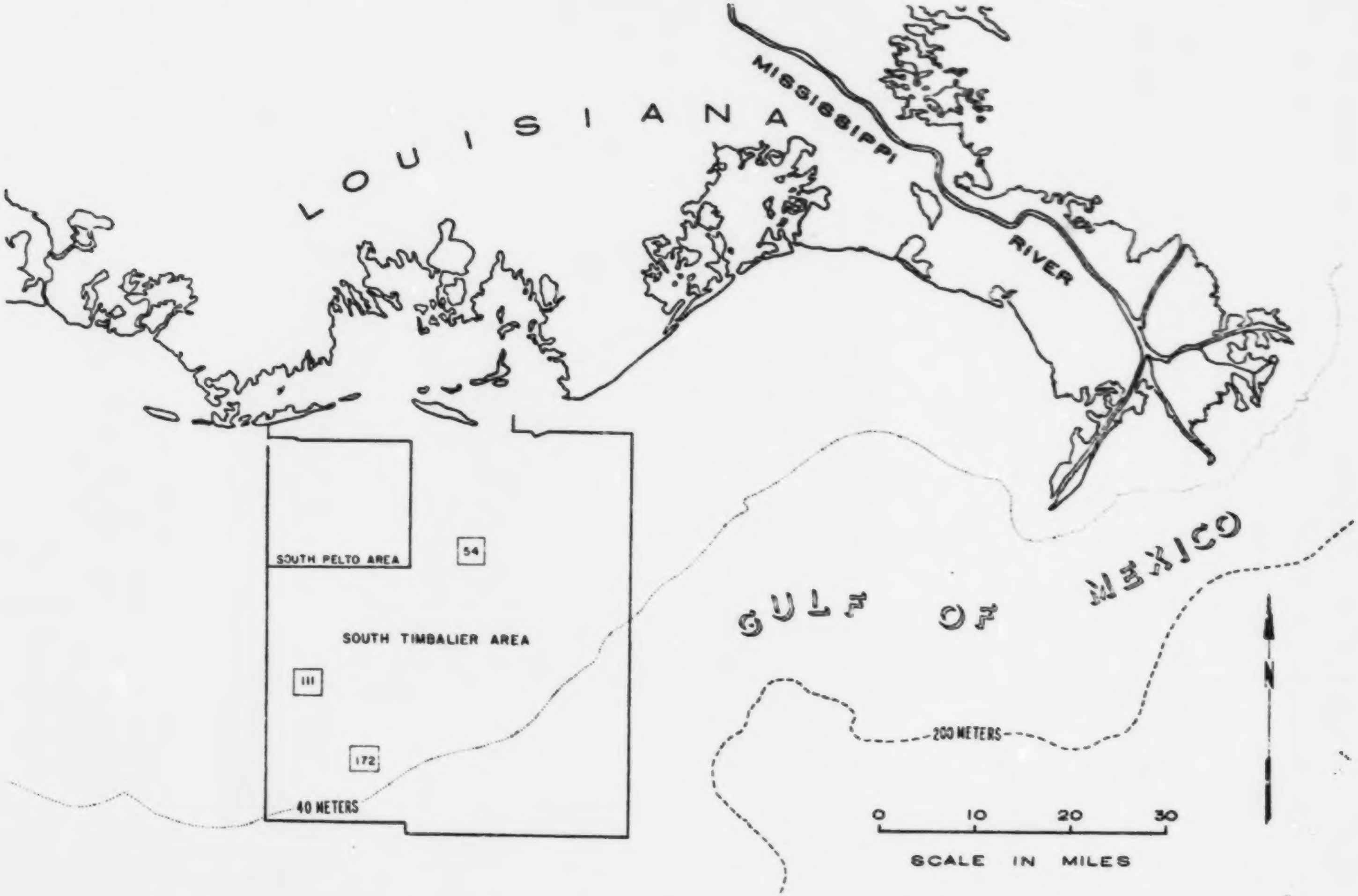
LOUISIANA
MISSISSIPPI
RIVER
GULF OF MEXICO
SOUTH PELTO AREA
54
SOUTH TIMBALIER AREA
111
172
40 METERS
200 METERS
N
0
10
20
30
SCALE IN MILES

Figure 2. Location map showing South Timbalier Area Blocks 54, and 172.

We were fortunate in that this was a time of low discharge of the rivers, that there had been no major storms in the Gulf, and the typical "muddy layer" was absent, so that the water was remarkably clear all the way to the bottom and good photographs could be taken. Figure 3, taken under the rig, approximately 70 feet from the upcurrent edge of cuttings, shows "normal" sea bottom for this area. As can be seen from the photograph this is an area of sandy mud which has been extensively burrowed by marine organisms. The photograph in figure 4 was taken approximately 25 feet from that in figure 3, and 50 feet from the cuttings. It shows indurated blocks of very fine sandstone of Pleistocene (?) age which have been exposed by normal scour activity of the sea in this area. These are similar in composition and hardness to much of the cuttings, but are a naturally occurring phenomenon.

Figure 3. "Normal" sea bottom, as seen under the Dixielyn 10 rig while drilling in 80 feet of water in South Timbalier Block 111. The sandy mud bottom is highly burrowed, and has some small mollusk fragments (white in the photograph). The hole in the mound in the center of the photograph is approximately 3 inches across.

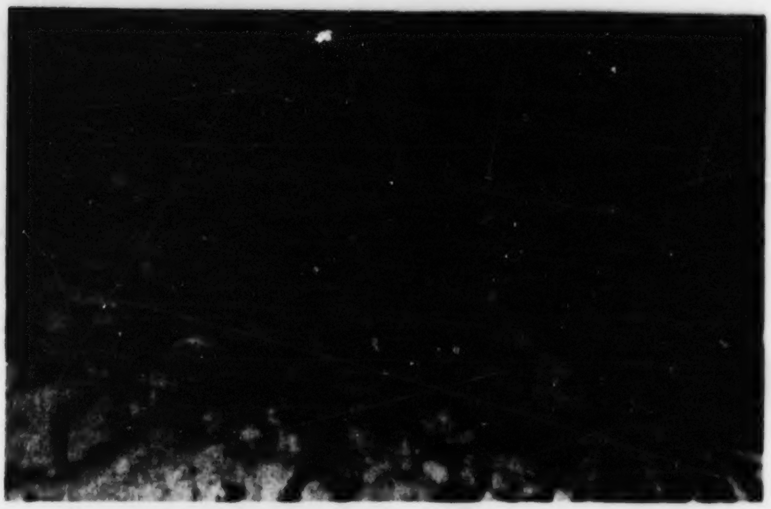

Figure 4. "Normal" sea bottom, taken approximately 25 feet from figure 3. The angular blocks are indurated, very fine sandstone of Pleistocene (?) age which have been exposed by natural scour activity of the sea in this area.

While the well was drilling and the cuttings coming down through the water, mobile organisms were moving around on top of the fresh cuttings pile. Small groupers and red snappers (figures 5 and 6) as well as other unidentified fish seemed quite at home on the new sea bottom. Several types and sizes of crabs were wandering about or were dug in (figure 7) on the pile. Even one small, slow-moving gastropod was observed. All seemed to be going about their business as they would had the rig not been there.

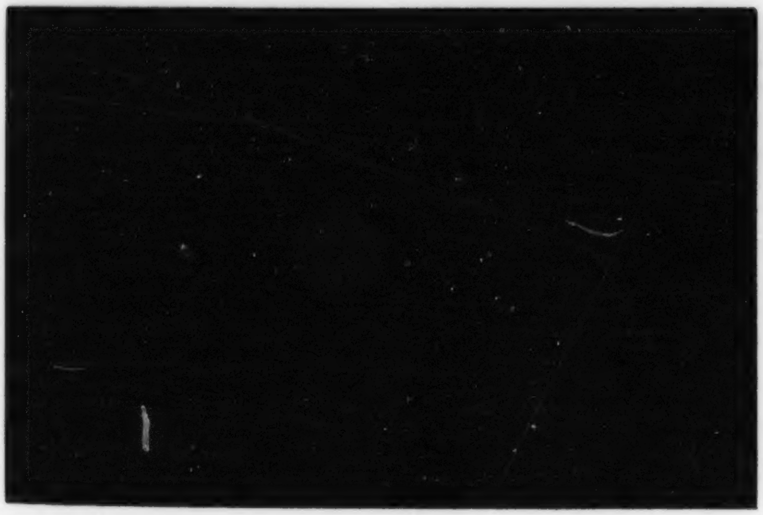

Figure 5. Surface at the center of the area of cuttings accumulation. Note the small fish at rest on the cuttings in the center of the photo, and other fish swimming in the background. Taken with a 15-inch closeup lense, thus the horizontal field of view is about 12 inches at the distance of the small fish. Individual cuttings or rock chips are readily discernible.

Figure 6. A red snapper is investigating a hole dug in the top of the pile of cuttings by the photographer. Most of the animals observed were engaged in their usual activities, and seemed unaffected by the drilling operations.

Figure 7. A small crab is using a large lump of hard clay for protection as he stirs up a cloud of mud while burrowing into the accumulating cuttings. Photo was taken with a 15-inch closeup lense.

Some people, with no firsthand knowledge of the sea bottom environment, have hypothesized that the surface of a pile of cuttings would be sterile for many years. Our experience and study indicates that that is absolutely not true. Both organisms and the sea itself begin to rework the cuttings as soon as they are deposited on the bottom. Shale chips, upon contact with the sea water, begin to disaggregate in a slow but continuing manner, eventually to become unconsolidated mud like that brought in by the rivers. Mobile benthonic organisms from the surrounding sea floor move up onto the cuttings and build homes as they would anywhere else, as do the larvae of sessile organisms. We had expected such from our knowledge of the faunas and of the physical effects of the sea; however, we have only recently obtained photographic proof.

The question had often been asked of us, what did the surface of a pile of well cuttings look like after the cuttings had been there for some time. In order to get a definite answer, we recently undertook a study of same at some of our platforms. It was our intention to use scuba gear to visit the site of a well that had been drilled within the last 1 to 1-1/2 years, measure the extent and thickness of the pile, observe the fauna or lack of fauna on the pile, and take sufficient photographs and bottom samples to demonstrate what was actually there, and to make comparisons to adjacent "undisturbed" areas. The time lapse noted above from drilling to observation was chosen as a period of time in which marine organisms could react to the presence of the cuttings, and yet be before the pile was redistributed or sank into the sea bottom. We chose South Timbalier Block 54 field since a well had been drilled at the desired time in the past, the water was of a convenient depth for diving (60-65 feet), and living quarters were available for support work.

Unfortunately, because of proximity to the Mississippi and Atchafalaya Rivers, each about 80 miles away, this area receives a large amount of clays, which are continually reworked by normal currents and swell, and by storm waves. As noted by Griffin and Ripy, Oetking et al., and Shinn (refs. 1, 2, and 3), this is an area that often has a well developed nepheloid layer, a layer of highly turbid water near and at the sea bottom. The nepheloid layer, also called the muddy layer or flocculent zone, contains a high percentage of clays and organic detritus in suspension. When we arrived in the area on January 8, 1975, the waves were only 3 to 5 feet high, but the entire area was somewhat murky near the surface and visibility was zero on bottom without a diver's light. In addition, there was a noticeable surge on bottom at a depth of 65 feet. Obviously, little examination of cuttings would be possible, if the pile could even be found.

A decision was made to move 20 miles further offshore into 110 feet of water in the South Timbalier 172 field. It was hoped that the increased water depth and the greater distance from shore would give us better visability on bottom. Gulf had drilled one well from a platform in block 172, with actual drilling completed by April 30, 1974, or approximately 8-1/2 months before we dove in the area. Here too, the bottom 20 feet of the water column was filled with suspended sediment. It must be remembered that this turbidity was due entirely to natural conditions, and not to any drilling activity in the area. The nearest well then drilling was in block 54, approximately 20 miles to the north, and had no effect on any but its own immediate area. Bottom water near that platform in block 172 was so murky that both the diver's face and his 100,000 candlepower light had to be within 6 to 10 inches of the bottom to be able to distinguish any features there.

The first dive near this platform was outside the area of any cuttings accumulation, and the bottom was typical of that of the Gulf--a thin surface layer of very soft and unconsolidated mud, underlain by sticky clay with some sand. The bottom was highly burrowed, and there were numerous whole and broken mollusk shells.

The second dive near the platform was on the pile of cuttings as was immediately evident by poking one's fingers in to the bottom and feeling the chips. However, that surface was also highly burrowed, and had whole and broken mollusk shells; indicating that numerous benthonic organisms have found this habitat quite suitable to their needs. It should be noted here that there was a thin accumulation of very soft and unconsolidated mud there (figures 8 and 9) as was true of the "normal" sea bottom, indicating that marine sediments are already covering the cuttings. Although the water was very murky, several photographs were obtained using a 4-3/4 inch Hydrophoto closeup lense on a Nikonos camera, with a Honeywell Strobonar 770 strobe for a light source. These photos (figures 8 and 9) show evidence of burrowing, small mollusk fragments, and some cutting chips that have either not been covered over, or have been reexcavated by faunal activity.

A sample was taken of the top 2 inches of sediment cuttings at that spot. The cuttings have been somewhat rounded by partial disaggregation of the clays from the swelling due to seawater adsorption and possibly from abrasive current action. These clay chips also show a brownish oxidation on the exterior, further evidence that the chips are undergoing weathering and will not remain as entities. Fossil foraminifers protruding from these chips are proof absolute that these are definitely cuttings from the well, and not from any possible local rock outcrop.

Figure 8. Surface of cuttings that had been on the sea bottom for 8-1/2 months, in 110 feet of water in South Timbalier Block 172. A number of chips are visible, but most of the surface is covered with mud accumulation from normal sedimentation processes. Dark, conical object in upper right is a live snail whose shell is covered with a fuzzy growth of algae and/or hydrozoans. Apparent slope of the bottom is due to the angle at which the camera was held. Photo was taken with a 4-3/4 inch closeup, and lateral field of view across the center of the photo is approximately 3-1/4 inches.

Figure 9. Photo taken approximately 3 feet from figure 8, and with the same lense. Light-colored objects are mollusk fragments.

A comparison of the included Recent fauna in that sample with that of a sample taken from "normal" sea bottom on the other side of the platform shows that both contain essentially the same fauna, and in essentially the same abundance. Present in both are nearly 30 species of foraminifers, more than 15 species of mollusks and micromollusks, several species of bryozoans (both free specimens and coating mollusk shells), echinoid spines, ophiuroid ossicles, crab fragments, etc. This is clear and undeniable proof that a number of types of benthonic organisms find the area of cuttings accumulation just as environmentally acceptable as the surrounding area.

Drilling Fluids

Another area of concern is the finely particulated and dissolved material put into the sea during drilling operations--primarily material which coats the individual chips and is washed off by the seawater. This would include finely divided mud, whether from the drilled formations or additives, and various chemicals which might be added to the mud system. Specifically, concern has been expressed over the effect of muddy water on filter feeders, and the possible toxicity of additives such as caustic, barite, and chrome lignosulfonate.

During the time we were in the area, a well was being drilled from Exxon's "E" platform in the South Timbalier Area Block 54 field. We sampled "clean" seawater 100 yards upstream from the platform as a standard, as well as the drilling mud in mud tanks below the shale shaker, the muddy water at the bottom end of the downpipe, and the water in the middle of the muddy water plume (at the sea surface and at minus 30 feet at distances of both 100 yards and 1/8 mile downstream from the downpipe). We would have taken samples further downstream but could not define any muddy plume further than that. All samples were collected in clean, 1-liter jars, which were immediately sealed.

A definitive test for caustic in the seawater can be made by measuring the pH. For all samples, pH measurements were made by measuring with a Beckman model N pH meter that was calibrated against solutions of known pH both before and after running the samples. The pH was determined again 4 days later at the Exxon Production Research Co. laboratory in Houston, Texas. As can be seen from table 1 and figure 10, discharge from the drilling operation had virtually no effect on the pH of the seawater. Greater variations in pH occurred naturally, due to water depth, than occurred from drilling fluids.

A comment should be made here concerning the pH of the drilling mud. Caustic was continually being added to the mud system so that the pH of the mud was 10.4 both going in and coming out of the hole. However, seawater was also being added to the mud system at the shale shaker, and magnesium ions in that water combined with the caustic to effectively neutralize it and bring the pH down to essentially that of normal seawater. Thus, the mud tank sample pH of 8.5 (sample no. 1 of table 1 and figure 10) reflects the action of the relatively small amount of added seawater on the caustic in the mud. The pH of the system was built up to 10.8 between where that sample was taken and where the mud was pumped back down the well.

Geochemists at EPRCo also determined the amount of suspended solids in each sample. Ascertained values as shown in table 1 and figure 10 indicate that although finely divided suspended solids do enter the sea, they are so diluted by the seawater as to be of no significance. It is of interest to note that the "clean" seawater upstream from drilling operations had essentially the same amount of suspended solids as did seawater 1/8 mile downstream. Unfortunately, the very murky water near the sea bottom, in the nepheloid layer, was not sampled. However, according to GURC studies (refs. 1 and 2), that water can have at least as much naturally occurring solids as does the water at the end of the downpipe.

The last few Environmental Impact Statements have directed some comments to the addition of chrome lignosulfonate, with the idea that it might contribute toxic amounts of soluble chromium to the sea. Spersene, one such chemical, had already been added to the E-54 well mud system in standard amounts. All samples collected were analyzed for chromium by

Table 1. Analyses of samples collected January 9, 1975, by R. P. Zingula et al., at and around a well being drilled at Exxon's South Timbalier Block 54-E platform

Sample No.	Description	Measured pH[a] on-site	Measured pH[a] lab	Suspended solids, mg/l	Soluble[b] Barium	Soluble[b] Chromium
1	Drilling mud from mud tanks under the shale shaker	8.48	8.5	350,000	<0.5 ppm	<0.2 ppm
2	Mud at downpipe at water surface	8.42	8.5	278	"	"
3	Water at center of muddy stream at sea surface, 100 yd downstream from downpipe	8.42	8.6	40.7	"	"
4	Surface water at center of muddy stream 1/8 mi downstream from downpipe	8.43	8.6	5.5	"	"
5	30 ft below sea surface at location of sample 3	8.20	8.4	1.5	"	"
6	30 ft below sea surface at location of sample 4	8.18	8.4	1.1	"	"
7	"Clean" seawater at sea surface, 100 yd upstream from downpipe	8.45	8.6	5.2	"	"
	Spersene solution[c] (lab.)	---	3.1	231	---	11,400 ppm

[a] Samples taken at 8-8:30 a.m., January 9. Onsite pH measurements made at 10-10:30 p.m., January 9. Lab measurements made January 13 & 14.

[b] Measurements of soluble chromium and barium were by atomic absorption, calibrated against a standard. Concentrations were below the limits of measurements of the system, i.e., 0.5 ppm barium and 0.2 ppm chromium.

[c] Spersene solution was made by mixing two parts water with one part spersene by weight and letting stand for 24 hours.

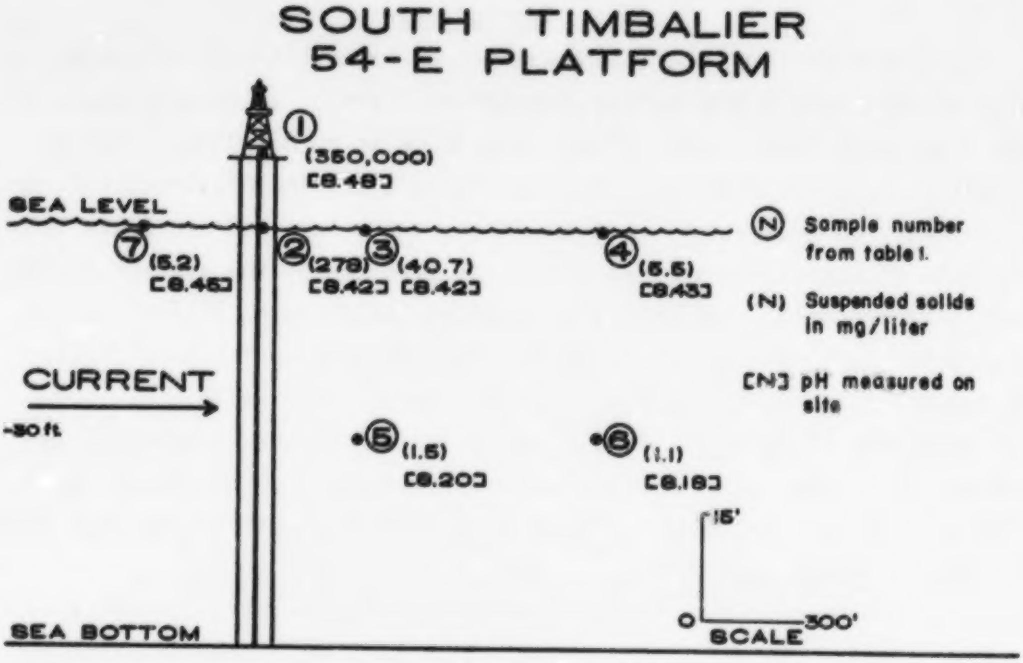
SOUTH TIMBALIER
54-E PLATFORM
①
(350,000)
[8.48]
SEA LEVEL
⑦ (5.2)
[8.46]
② (278)
[8.42]
③ (40.7)
[8.42]
④ (5.5)
[8.43]
Ⓝ Sample number from table 1.
(N) Suspended solids in mg/liter
[N] pH measured on site
CURRENT
-30 ft
⑤ (1.5)
[8.20]
⑥ (1.1)
[8.18]
15'
0
300'
SCALE
SEA BOTTOM

Figure 10. Diagrammatic presentation of pH and suspended solids in samples described in table 1.

the atomic absorption method calibrated against a standard. As noted in table 1, any chromium that was present in the mud systems and in the muddy seawater was less than 0.2 ppm and too minute to be detectable. Although the atomic absorption technique is not accurate enough to detect amounts of chromium as small as would typically be present in seawater, it does indicate that there is no large amount of chromium entering the sea from such drilling operations. As also noted in the final Mafla EIS, there are no known hazards to the environment from chromium in the very diluted form in drilling mud.

Tests for soluble barium were also run, even though the barite added to the drilling mud is considered insoluble. As can be seen from table 1, no detectable amounts of soluble barium were present in any of the samples. At the same time, it should be noted that barium sulfate is the twelfth most common mineral compound found in seawater.

Conclusions

Offshore drilling operations are not as harmful to the marine environment as some people have either proposed or feared. In the Louisiana offshore and many other areas, rivers contribute so much sediment that any resulting from drilling operations is negligible. The Mississippi River alone dumps as much weight (and many times the volume) of sediments into the Gulf of Mexico every 51 seconds as is produced by the average 10,000-foot offshore well. Additionally, trawling and dredging activities coupled with the naturally occurring nepheloid layer keep far more solids in suspension than those supplied by all the drilling wells.

Cuttings accumulating on the sea bottom do not create deserts, as suggested by some. Mobile organisms are active on the surface of the pile even while drilling is going on; and in a few months' time they turn it into a "normal" sea bottom.

The common chemicals normally used in drilling--caustic, barite, chrome lignosulfonate, etc.--are present in such small quantities that chemical interaction and dilution should make their effect negligible (table 1).

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DISCUSSION

MR. DENNIS G. WRIGHT (Environment Canada, Winnipeg, Manitoba, Canada): I have just a comment.

In the past 2 days we have been discussing drilling wastes. Nobody has really come out with a statement of just how much waste we are talking about. My question is, has anybody in the industry taken a look at just how much drilling fluid you are wasting to the environment?

DR. ZINGULA: Yes and no. I would like to say not that we are wasting to the environment but that we are putting over a given amount.

I think Jim Ray, who will be speaking tomorrow, has some figures on that in his paper.

I would like to throw in one little comment. I know your rivers, and so forth, up there in Canada are a little colder, because I am used to scuba diving up there, too, and they are not carrying as mucn sediment as the Missisppi River. But out here the river puts in to the environment every 51 seconds the amount of sediment in weight (not volume, because our volume is smaller) that we would put in from a 10,000-foot well. But Jim Ray will have figures tomorrow on what is typical for a 10,000-foot well in volume and weight of the sediments and the various mud components.

TREATMENT AND DISPOSAL OF WASTE FLUIDS FROM ONSHORE DRILLING SITES

G. A. Specken*

Abstract

The accumulation and storage of waste materials in open, earthen pits (sumps) during the drilling of onshore oil and/or gas wells leads to an appreciable volume--up to about 100,000 barrels per site--of waste fluids of varied composition. Disposal of these sump fluids has become a problem in those parts of the country where regulatory bodies no longer allow simple dumping of the fluids to the environment. For instance, in Western Canada the clarified water from drilling site sumps must meet certain quality standards, primarily the passing of a trout bioassay before it can be pumped off-lease. A process has been developed whereby the sump contents are treated in situ such that a major portion of the total fluid volume is generated as clarified, detoxified water acceptable for off-lease disposal to the land. A minor portion of the total fluid volume is left wet, flocculated solids or sludge in the bottom of the sump pit for burial there or disposal to the lease area. The various aspects of this treatment and disposal process are discussed, and cost data for 2 years of commercial operation in Western Canada are presented. In some selected cases, the cost data are related to the types of drilling fluid systems used to drill the holes.

INTRODUCTION

In order to appreciate various aspects of the treatment and disposal of waste fluids from onshore drilling sites, a brief examination of past and present practices in Alberta in this regard is helpful.

During the drilling of an onshore oil and/or gas well, an open earthen pit or sump is used as a collecting basin for waste drilling fluid,

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solid cuttings from the hole, and wash water from the drilling rig deck. Because the pit is open to the atmosphere, the sump contents are increased or decreased by whatever net precipitation happens to occur. By the end of a drilling operation, an appreciable volume (typically 5,000 to 50,000 barrels, and occasionally as much as 100,000 barrels) of waste fluids has thus accumulated in the sump. Generally, sump contents consists of three distinct phases--a thin layer of oil scum on the surface, a large aqueous phase with dissolved components and suspended solids, and a bottom layer of sludge containing most of the solids which have settled.

Until recent years, it was normal practice in Alberta to dispose of the contents of drilling site sumps directly to the environment, that is, to the lease and surrounding area, without any prior treatment whatsoever. If the oil scum was inflammable, it was not uncommon to concentrate it at one end of the sump and burn it. The so-called "clear water" layer was pumped out of the pit and distributed over the lease or adjacent area to dry to atmosphere or soak into the ground. The partly empty pit was then filled by bulldozing brush and earth into it. In doing so, the sludge layer was either buried, or "squeezed" out of the pit and spread on the lease surface to dry or be worked into the topsoil.

In recent years, public and governmental concern over environmental pollution led to more stringent requirements than those outlined above for the disposal of these waste fluids. By the early 1970's, there was a significant number of cases in Alberta where the sump fluid in question was considered environmentally hazardous and it had to be hauled away and disposed of in some designated location, such as a gravel pit or a disposal well. The high haulage costs and the long time delays for the total lease cleanups pointed to the need for a better disposal method for these "problem" sumps. Consequently, in mid-1971, Wilson Mud Service Ltd. initiated a research project to achieve this end.

DEVELOPMENT OF THE TREATMENT PROCESS

The ultimate objective of the research project was to develop a process by which drilling-site sump fluids could be altered so that they could be disposed of directly and safely to the environment. Under the project, it was proposed to evaluate various water and wastewater treatment methods and apply them to drilling-site sump fluids in the context of remote drilling locations.

For the project evaluation, the total process was divided into three areas of investigation, namely oil-water separation, solids-liquid separation, and purification of the clarified water phase to render it sufficiently innocuous to the environment. Consideration of the various constraints imposed by the drilling-site context led to a specific list of known treatment methods to be evaluated in each area of investigation. Although these proposed methods were part of existing technology, the various aspects of the drilling site context--remote location of leases, seasonal weather conditions, complex and variable sump composition, and diversity in water quality required by regulatory bodies--suggested that existing treatment methods would require some adaptation and innovation.

The various candidate processing steps were first screened for technical and economic feasibility by conducting paper engineering studies supported by experimentation, where necessary, on actual problem sump fluids. At the outset, it was evident that only batch-type processes or treatment steps that could be effected right in the sump were the most promising candidates. Also, a relatively small scale of testwork--batch charges of a quart to a gallon each--was found satisfactory for evaluation of certain steps (such as coagulation-flocculation, adsorption, precipitation, and oxidation). This was because the efficacy of these techniques is usually predictable, provided that adequate mixing and/or contacting with the test fluid is achieved. The importance of this small-scale development work is emphasized, because it led to full-scale field tests without intermediate scaleup.

The experimental program involved as large a variety of actual problem sump fluids as possible, so that the resultant process would be versatile enough to cover the majority of problem sumps, if not all, when commercialized. It was anticipated that one water treatment method would be insufficient to cover the range of pollutants known to exist in sump fluids, but it was intended to engineer all the chosen techniques into one equipment assembly. This was borne in mind when selecting the various treatment methods, most of which can be effected by pumping and mixing some ingredient into the sump contents.

On the basis of the engineering studies and the bench scale experimentation program, the most promising candidate processing steps were translated into a prototype field equipment assembly, which was then used to conduct a field test program. After five successful field tests, a followup evaluation of the process and the prototype unit was carried out.

In both the bench scale experimentation program and the field test program, samples of treated and clarified water from each experiment were evaluated in terms of water quality by the test(s) that would be used by the pertinent regulatory bodies in a real disposal situation. In Alberta, the main water quality test, developed especially for this purpose, is a modified fish bioassay using rainbow trout. Therefore, the treatment process was designed primarily to transform a maximum amount of a given sump fluid into clarified, detoxified water that passes a trout bioassay.

COMMERCIAL APPLICATION OF THE PROCESS

The process that evolved from the above research project has been applied commercially in Alberta during the operational seasons of 1973 and 1974, and to a lesser extent in British Columbia in 1974. An operational season is generally limited to the time between spring thaw and fall freezeup, but has been extended a month or so beyond freezeup by using heating equipment to melt ice caps or keep them from forming on the sumps while the various steps of the process are underway.

A rather methodical approach is taken in the commercial application of the process. For a given sump, this involves a series of activities that include a prior sump evaluation, a cost projection and contract bid, and the actual field treatment and disposal of the fluid.

1. Sump Evaluation

In order to insure that a given sump can be treated successfully and disposed of at a predictable cost, a complete evaluation of it is carried out. This evaluation takes place both at the sump site and in the laboratory.

First, the location is visited to obtain direct information on the sump, the lease, and the surrounding area. The surface dimensions of the sump are measured. Using a boat to traverse the surface of the sump, depth measurements are taken (by probe or weighted string) from various points so as to estimate both the average total depth of fluid in the sump and the average thickness of the mud layer in the bottom of the sump. Similarly, with the boat located at different points on the sump surface, fluid samples are taken from different elevations in the sump. The existence and approximate volume of an oil layer are noted, as well as the relative degree of solids suspension in the fluid body. Finally, a visual appraisal is made of the lease access road, the surface condition of the lease, and the surrounding area. This helps to predict what mobility problems might be encountered, and also indicates where the service rig could be located next to the pit and where the treated water could eventually be pumped.

The laboratory evaluation involves treatments of the sump samples to determine the proper sequence and dosages of chemicals required for successful toxicity reduction and clarification of the sump fluid. The efficacy of each treatment program thus determined is verified by trout bioassays on the lab-treated samples. Certain analyses are done on both untreated and lab-treated samples to enable prediction of various ion concentrations and pH of the final water.

The thorough sampling procedure of the field evaluation (which invariably yields two to four dozen quart samples of fluid from each sump), coupled with some simple analyses on the individual samples in the laboratory, has proven time and time again that sump fluids tend to become stratified. This is especially true of sump fluids containing a high concentration of suspended solids. A typical example of a stratified sump is illustrated by the data in table 1, in which the results of calcium, chloride, and pH determinations are listed according to sample depth. The data show that all three--the calcium content, the chloride content, and the pH of the fluid--increase remarkably with increasing fluid depth, and that the ions appear to be associated with the suspended solids. Similarly, it

Table 1. Selected analyses on samples according to depth

Sample elevation	Sample point	Sample appearance	Ca, ppm	Cl, ppm	pH
surface	12	almost clear	300	1650	7.1
3 ft depth	2	almost clear	320	2330	7.4
	5	almost clear	360	2720	7.2
	7	almost clear	360	2820	7.5
3 ft average	--	--	350	2620	7.4
6 ft depth	4	almost clear	480	6800	9.2
	9	almost clear	500	7000	9.2
6 ft average	--	--	490	6900	9.2
8 ft depth	3	almost clear	560	7000	9.3
10 ft depth	1	light solids	600	7000	8.2
	6	high solids	5360	11650	9.6
	8	high solids	400	6900	10.6
	10	light solids	680	6600	10.9
	11	light solids	560	6700	9.2
10 ft average	--	--	1520	7990	9.7

can be shown that the level of dissolved, toxic organics in a surface sample can be radically different than that in a depth sample. This wide variation in fluid composition in a stratified sump is emphasized, because it points out the necessity of the multisample approach, so that a composite sample can be made up to represent the majority of the fluid body in the sump.

2. Cost Projection and Contract Bid

Based on the information of the sump evaluation(s), the total cost to treat and dispose of the sump fluids on a given lease is estimated. This cost projection can be influenced appreciably if contracts to treat other sumps in the same general area have been won, in that optimum scheduling of equipment and crew reduces the projected cost per contract.

The total treatment and disposal cost is always specified on a contract bid, although the cost expressed in cents per barrel of the total fluids to be treated can be determined from the information in the sump evaluation.

3. Field Treatment and Disposal

The total sump treatment and disposal process can be broken down into five operations--oil removal, prior clarification, water detoxification, final clarification, and pump-out.

Removal of oil from a sump is necessary, not just to facilitate the subsequent toxicity reduction step, but to make it economically feasible as well. In most cases, the residual volume of oil in a sump after the oil removal step should be as low as a barrel or less. The quickest and cheapest method of oil removal is to burn it on the surface of the fluid body. If permission to do so cannot be otained from the regulatory bodies, usually because a real fire hazard to surrounding vegetation exists, then it is necessary to skim the oil from the sump. In addition to provision of light mechanical equipment for this skimming and removal operation, a liquid surfactant is sometimes used to assist in moving the oil across the surface of the water. The oil scum removed from the sump is preferably put into a small auxiliary pit for subsequent burial there, or for ultimate spreading and mixing into the topsoil on the lease.

A prior clarification step is necessary if the concentration of suspended solids in the fluid body above the settled mud layer is considered too high, in anticipation that the suspended solids would interfere with the chemicals used in the subsequent detoxification of the water phase. Clarification of the sump water is accomplished by a flocculation step followed by a period of time sufficient to allow settling of the flocculated solids to the bottom of the sump. The flocculation step is carried out by dispersing coagulants and flocculants (polyelectrolytes) into the sump water at predetermined concentrations. A truck-mounted equipment assembly, consisting primarily of a pumping and solutioning unit, and a floating sump mixer are provided to effect this step. The truck-mounted units can recirculate the sump contents at rates up to about 3,000 barrels/hour, while the floating mixers can turn the sump contents over at rates up to about 9,000 barrels/hour. Depending on the original solids concentration in the sump and the "tightness" of the solids sludge after settling, usually about 60 percent of the total fluid body is obtained as a solids-free water layer.

If a sump has been classified as toxic, in that an untreated sample of it has failed the trout bioassay, then it must be treated to reduce the level of toxic components dissolved in the water. This is done by thoroughly mixing treatment chemicals into the body of fluid using the truck-mounted unit in conjunction with a floating sump mixer. In addition to removal of dissolved toxic components from the water, it is sometimes necessary to adjust the pH of the water so that ultimately it will pass a trout check. Choice of the kind of acid for pH-adjustment is important, so that the concentration limit on the anion added (chloride, sulphate, or phosphate) is not exceeded.

A final clarification step is always required after the detoxification step in order to remove any residual suspended solids and thus produce the clarity required for off-lease disposal of the treated water. As described above, clarification is accomplished by coagulation-flocculation and sedimentation of the solids.

After the detoxification and clarification steps have been completed, a representative sample of the final water to be pumped out is taken for a final trout bioassay and water analysis. These tests are done at a certified commercial laboratory or at the Alberta Energy Resources Conservation Board laboratory, but in any event, the results of the tests are made available to the pertinent regulatory body personnel. Because a successful trout check requires 4 days, there is usually a time lapse of at least a week between the final clarification step and the pump-out step.

Pump-out of the clarified, treated water from a sump is done only after permission is obtained from the regulatory bodies and very often is done under their surveillance. Because it is invariably desired to pump the water on the land adjacent to the lease, the applicable regulatory body and/or land owner is approached ahead of time so that the exact area for disposal is agreed to by all parties. Two methods of pump-out have been offered--one using open-gated irrigation hose, and the second using an irrigation gun (sprinkler). The open-gated irrigation hose is the preferred pump-out method because of its higher disposal rate (about 3,000 barrels/hour) for the horsepower provided, and in 2 years of commerical operation it has always been used for the pump-out step.

There are certain practical considerations that place limitations or constraints on the use of the process. Because the sump contents must be in the fluid state to undergo the various operations, the process is a seasonal one, in that use of it is generally limited to the time between spring thaw and fall freezeup. Accessibility both to the lease and to the sump is essential for each processing step. Usually these steps are spaced across a time span of more than 2 weeks, with several trips to the lease involved. The service rig must be able to park within about 15 feet of the sump, and vehicular mobility on the lease is required to some extent for all the processing steps.

The primary feature of the treatment process is its ability to reduce the level of dissolved, toxic components and suspended solids in the sump water so that the trout check can be passed. The process does not lower the chloride content of the water. Therefore, if the initial chloride concentration of the untreated water already exceeds the limit set by the regulatory bodies for disposal in a given area, then disposal of the treated water, even if the trout check is passed, may still be a problem.

COST OF THE PROCESS

Selected statistics and cost data on all the sumps treated and disposed of by Wilson Mud Service Ltd. in 1973 and 1974 are presented in table 2. From this data, it appears that the overall average cost of the process is in the order of 30 cents per barrel of sump fluids treated. However, as table 2 also shows, the cost varied widely, from below 20 cents to above 50 cents per barrel of fluids treated.

This treatment cost variation can be traced to various contributory factors, such as sump size, the number of sumps per lease, the remote locations involved, and especially the nature and varied composition of the

Table 2. Selected statistics and cost data on treated sumps

	1973	1974
Number of treatment-disposal contracts	15	22
Total fluids volume per lease, (barrels)		
-average	33,200	34,000
-range	3,000 to 74,000	12,000 to 75,000
Volume pumped out, (% of total treated)	62.5	51.9
Depth of well drilled, (feet)		
-average	12,260	11,550
-range	6,400 to 18,000	7,280 to 18,530
Total fluids volume, (barrels), per foot of hole drilled	3.02	2.95
Total treatment & disposal cost, ($), per contract		
-average	9,220	10,420
-range	1,500 to 20,000	1,500 to 34,000
Total weighted cost, (¢/barrel) of treated fluid		
-average	27.8	30.6
-range	17.1 to 57.8	13.5 to 61.5

fluids themselves. The effect of some of these factors on treatment cost can be shown by segregating the treatment contracts of 1974 into two categories, one in which no special problems were apparent and in which the treatments were considered "typical", and the other in which two factors (the nature of the fluids, and very remote locations) obviously increased the cost and the treatments were considered "nontypical". This has been done to derive the statistics and cost data displayed in table 3, where the "nontypical" contracts of 1974 include four sumps containing invert drilling fluid systems, one sump containing a modified lignite drilling fluid system, and two sumps remotely located in British Columbia. The data of table 3 show that the average treatment cost (at about 44

Table 3. Selected statistics and cost data on treated sumps (segregation of 1974 contracts)

	1974 Treatment Contracts	
	Typical	Nontypical
Number of treatment-disposal contracts	15	7
Total fluids volume per lease, (barrels)		
-average	31,200	40,100
-range	12,000 to 75,000	19,000 to 66,000
Volume pumped out, (% of total treated)	48.1	58.4
Depth of well drilled, (feet)		
-average	10,520	13,740
-range	7,280 to 16,910	8,900 to 18,530
Total fluids volume, (barrels), per foot of hole drilled	2.97	2.92
Total treatment & disposal cost, ($), per contract		
-average	7,090	17,540
-range	1,500 to 13,300	6,400 to 34,000
Total weighted cost, (¢/barrel) of treated fluid		
-average	22.7	43.7
-range	13.5 to 33.6	32.3 to 61.5

cents per barrel of fluid treated) of these seven special problem sumps is almost double that (at about 23 cents per barrel of fluid treated) of the other 15 contracts. The higher treatment cost of these special problem sumps was despite their larger sump size, which normally tends to decrease the cost expressed in cents per barrel of fluid treated.

Based on the cost projections arising from about 120 sump evaluations done to date, and on the actual costs of 42 contracts completed successfully in the field, it can be concluded that the one factor that has the greatest influence on a sump treatment program, and therefore the treatment cost, is the nature of the drilling fluid system used to drill the well. In general, the cost projected to treat sumps derived from either an invert or a KCl-polymer drilling fluid system is in the order of 35 to 40 cents per barrel of fluid treated, whereas the cost projected to treat sumps derived from various freshwater-gel systems is about 30 percent less. These particular drilling fluid systems are mentioned, because they are the ones that generally have been encountered in the sumps evaluated to date.

DISCUSSION

MR. RICHARD S. SCALAN (University of Texas, Austin, Texas): I admit you have a problem up there in Canada. But in South Texas, I wonder if the thing to do, in light of the gentlemen from GURC and Exxon, would be simply to put it on a barge, take it out to sea, and dump it?

MR. SPECKEN: Well, of course, we are discussing onshore disposal in a certain area. It seems that down in Texas you do not have the same volume of water involved in your pits. If anything, you are happy to get any kind of water on the land.

In Alberta we have the head waters of all of our rivers forming in those foothills, and I imagine this is one of the reasons why the regulations have evolved.

MR. DENNIS G. WRIGHT (Environment Canada, Winnipeg, Manitoba, Canada): Are you allowed to discharge any of your clarified waste to surface waters?

MR. SPECKEN: Yes, but only if we get the permit to do so from the Alberta Department of Environment. It takes longer, you have more analyses to present to them, and it has to be a special case. But it can be achieved, yes.

MR. WRIGHT: I see. Does your process reduce chloride concentration in any way?

MR. SPECKEN: Definitely not. You can reduce some of the ions, perhaps phosphate if you have to, but chloride is not reduced and, therefore, what is there you are stuck with.

There again, limiting the amount of water in a pit usually works the wrong way, because more water decreases the chloride concentration.

THE TOXICITY OF DRILLING FLUIDS, THEIR TESTING AND DISPOSAL

D. R. Shaw*

Abstract

The composition of drilling fluids is often complex, and the various components and combinations of chemicals are frequently quite poisonous. By the time the well is completed these materials have been relegated to the sump where they become a disposal problem. A method of sampling and testing has been outlined, so that the toxicity of sumps can be determined. Guideline outline appropriate action to be taken by the operator and the Government agencies to insure that fluids are disposed of by methods which affect the environment as little as possible.

SUMP FLUID COMPOSITION

Drilling fluids may be clay in water suspensions, or they may be progressively more complex or specialized for deeper wells. Modifications may include the addition of chemicals to raise or lower the viscosity and gel-strength, or adjust wall-building characteristics. The chemicals may be simple, like bicarbonate of soda, or very complex, particularly if the mud must be adjusted with emulsifiers or partially emulsified oil, bentonite extenders, thickeners, etc. A recent count of the brand name additives on the market exceeded 600.

A deep well may encounter soluble minerals such as salt, anhydrite, or phosphates. These materials dissolve into mud, usually necessitating the addition of special chemicals to offset the effect of the dissolved material. High temperatures of deep holes also necessitate the use of special chemicals in the mud system. Portions of all of these fluids and therefore portions of everything used in the drilling fluid or on or about the rig will find its way into the sump. The final fluid may then contain:

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(a) bentonites, drilled shales and minerals such as salt and anhydrite;

(b) formation fluids such as brines or crude oil;

(c) Mud additives such as:

  (1) thinners like quebracho, tannins, lignins, and sulphonates;

  (2) viscosifiers such as carboxymethylcellulose;

  (3) emulsifiers like detergents and soaps;

  (4) completion chemicals such as frac-fluids and acids;

  (5) coagulants like the polyacrylamides;

  (6) emulsified oil - crude oil or asphalt or diesel;

  (7) special chemicals for drilling mineral beds;

  (8) chemicals to stabilize emulsions;

  (9) chemicals to decrease heat susceptibility;

  (10) preservatives like Dowicide G and formaldehyde.

(d) rig wash compounds, and housekeeping chemicals;

(e) yard drainage, and spills of lubricating oils, diesel fuel, glycol, etc.;

(f) drilled cement, accompanied by chemicals used to minimize the effect of cement on drilling fluids.

SUMP FLUID TOXICITY

Experimental work done at the Energy Resources Conservation Board Laboratory indicates that many of the chemicals used in drilling fluids are toxic to plant and animal life. Some are synergistic with other commonly used or frequently spilled compounds. Synergism is the ability possessed by certain pairs of compounds such that they mutually cooperate to produce an effect greater than the sum of the effects produced by each component alone. A few of the materials used in drilling fluids are either not toxic, or are only toxic in very high and seldom used concentrations. A very few inorganic salts appear to be antisynergistic. The determination of all of the synergistic and antisynergistic effects of the millions of possible combinations that could be produced by mixing some of the more than 600 additives would be interesting but virtually impossible to produce. A number of the more important components and combinations of components have been tested in water using rainbow trout. Based on these tests the following generalizations seem to be justified:

(a) Some hydrocarbons such as crude oil produced from formation tests may not be lethal until the concentration is over 400 mg/l;

(b) Some detergents such as rig-wash compounds are not lethal until the concentration is over 200 mg/l;

(c) Many of the oil and detergent combinations that separately are lethal at fairly high concentrations are extremely lethal as mixtures when quite diluted;

(d) Stable suspensions of colloidal material (like the bentonite of the drilling mud) are lethal to fish, because they coat and suffocate them. The clear fluid extracted from some bentonite suspensions of 10 lbs/bbl (28,570 mg/l) of bentonite were not lethal to rainbow trout in 96 hours;

(e) Diesel fuel from fuel spills and machine cleanup, depending upon the method of manufacture, may be very toxic;

(f) The clear water extracted from a diatomaceous earth slurry as used in drilling muds is not toxic even when the slurry used 5 lbs/bbl (14,285 mg/l);

(g) A particular brand of reagent-grade KCl was quite lethal at concentrations as low as 1 mg/l. This was unexpected, since sodium salts are not toxic below 20 mg/l. KCl is used in special drilling muds;

(h) Ammonium phosphate and ammonium sulphate, which are used in drilling muds to inhibit clay swelling, are both toxic at the same low concentration. This should be expected, since ammonia is dangerous to most animal life at quite low concentrations, (less than 100 mg/l);

(i) Many of the polyacrylamide bentonite flocculants or extenders used in drilling fluids are not toxic at low concentrations (below 100 mg/l). This is well within the effective range;

(j) Corrosion inhibitors from drilling muds or packer tests are generally very toxic (in the same toxicity class as bacteriostats, which they resemble in structure);

(k) Soil sterilants and weed poisons used on the lease are often very toxic to animals, being in the less than 1 mg/l class;

(l) Some humic acid mud thinners are toxic at very low levels of concentration;

(m) Carboxymethylcellulose used in drilling muds as a viscosifier or water loss additive generally is not toxic until beyond the normal usage concentration (possibly because food grades are marketed for use in drilling fluids);

(n) Tannin-type mud thinners tend to be less toxic than other thinners (provided that they are tannins and not mixtures containing other materials);

(o) Food-grade glycols and some of their polymers, which could be used in special muds or as motor antifreeze, may be only very slightly toxic (20 lbs/bbl or 57,140 mg/l);

(p) Some of the polyethyleneoxy types of detergents or dispersants usable in drilling fluids or as rig-wash compounds are only slightly toxic. Some closely related compounds are quite toxic;

(q) Aluminum salts, trivalent metal salts, and alums, which may be used to clarify sumps, may produce a very toxic solution if the pH is not carefully controlled. The result is that the metal salt that would normally precipitate will remain in solution;

(r) Some lignosulphonate mud thinners are toxic at concentrations exceeding 100 mg/l;

(s) Some of the phosphoric acid ester dispersants, which could be used in drilling fluids or for rig-wash compounds, are toxic above the 10 mg/l level;

(t) Rape seed oil, which could be used to replace the more poisonous oils in drilling muds, is nearly nontoxic (provided that the edible variety--low in erucic acid--is used, and that surface active agents or detergents are absent);

(u) The clear water extracted from barium sulphate mud-weighting material is not toxic;

(v) Powdered gilsonite used in oil emulsion muds is not toxic in concentrations below 0.33 lb/bbl (about 1000 mg/l);

(w) Emulsion breakers used in muds seem to be very toxic, in the same class as some corrosion inhibitors and bacteriostats. Some may have similar structures;

(x) Sodium lauryl sulphonate used as a washing compound produces very toxic solutions at low concentrations.

SUMP FLUID DISPOSAL STANDARDS

As stated, sump fluids, since they contain the mud chemicals as well as rig spills of diesel fuel, floor washing detergents, testing chemicals, and formation fluids, have a very good chance of being toxic. When the well is completed or abandoned, the sump fluids must be evaluated and disposed of accordingly. Realizing the disposal problem, the Energy Resources Conservation Board, the Department of Energy and Natural Resources, and the Department of the Environment, all of the Province of Alberta, have jointly developed requirements for the treatment and disposal of drilling sump fluids, directed toward minimizing undesirable environmental effects.

The requirements respecting the testing, treatment, and disposal of well sump fluids have been developed although they are not yet issued. They will:

(a) Permit subsurface disposal to deeper formations that are not locally commercially productive of oil or gas, and contain no water having less than 20,000 ppm total dissolved solids;

(b) Permit surface disposal to the lease, provided that the total volume for disposal is less than 6,000 barrels, and that the lease is more than 300 feet from a stream, lake, or fresh water water well. Disposal to certain leases may be prohibited even if the preceding criteria are met, if in the view of the Government representative the lease will not accept this amount of fluid without runoff, or the fluid may migrate further than 300 feet to a body of water or freash water well;

(c) Permit off-lease disposal to the land surface provided that the sump fluids meet with the following criteria:
    (1) they contain less than 1,000 mg/l of chloride ion,
    (2) they contain less than 2,000 mg/l of sulphate ion,
    (3) they contain less than 4,000 mg/l of total dissolved solids,
    (4) the pH lies between 5.5 and 8.5, and
    (5) trout survive 96 hours in the clear aerated fluid;

(d) Permit disposal of sump fluids to water only if suitable land surface for disposal is unavailable.

Except for surface disposal to the lease area, the approval of a representative of the appropriate Government Department is required before the fluids may be disposed of.

The effects of chloride, sulphate, and other dissolved solids on vegetation are fairly well known (ref. 1). The concentration limits set out in the criteria are sufficiently low to minimize toxic effects on most plants. However, little is known of the effects on vegetation of the vast array of chemicals found in sump fluids. Approval to dispose of sump fluids to the land surface is also subject to passing a test using rainbow trout. This requirement is based on the fact that even though fluid is disposed of to the land surface, it may eventually find its way to streams and lakes. Trout, being accepted as a test species (ref. 1) and generally native to inland waters, into which sump fluids may flow, were therefore chosen as toxicity indicators. Furthermore, rainbow trout are readily obtainable from fish hatcheries.

The disposal criteria will be reviewed in one year. Further studies may also be undertaken to determine the effects of sump fluids on vegetation.

EVALUATION OF SUMP FLUIDS

In order to conform to the disposal standards, sump fluids that are to be disposed of off-lease must be sampled, analyzed, and a treatment program developed. With respect to these matters the following should be considered:

(a) Sampling - In order to evaluate a sump fluid it must first be sampled. Due to the colloidal nature of bentonite, coupled with a specific gravity above that of water, the sumps are almost never uniform in composition throughout. It is therefore necessary to take many samples from various places at several depths. Each of these samples will usually be found to have a quite different analysis, without any predictable chemical relationship to the nearby sample. A composite sample should be taken, mixed thoroughly, and then tested to determine certain key parameters;

(b) Preparation of sample - Before analysis, the bentonite must be flocculated so that a clear fluid can be obtained. If the bentonite is left in suspension, chemical as well as biological tests will be masked or changed. Generally the calcium ion (from $CaCl_2$ or $CaSO_4$) is effective in reducing the electrical charge or Zeta potential, when followed by the addition of an organic polyelectrolyte, which usually "tightens up the floc" so that a clear fluid may be readily produced. Notes of the amounts used to produce an acceptable sample should be kept so that this information can be applied to determine the concentration of chemicals needed to flocculate the sump fluid in the field;

(c) Chemical analysis - The clear fluid may now be analyzed to determine the pH, chloride, sulphate, and total dissolved solids. If the criteria are met, disposal may proceed according to the guidelines;

(d) Biological testing - While the chemical analysis is taking place, another portion of clear fluid is subjected to testing with live rainbow trout in accordance with sound testing procedures (ref. 2). This is done because there is NO single chemical test or group of chemical tests that will indicate whether a fluid is toxic or not. A live animal will be influenced by its total environment, therefore testing the fluid with live trout should show synergistic actions or other untoward total effects caused by all the chemicals in the fluid. As testing sump fluids proceeds, there are two misconceptions which begin to be believed:

    (1) The belief that if the pH is near 7 and the chloride ion concentration is low, then the fluid is most likely to be nontoxic. Few statements could be as wrong as this.

(2) The belief that if trout survive the test for 4 days, then the fluid is nontoxic. This is also incorrect. The fluid may be judged as relatively nontoxic, since the fish did not die quickly, but the test fish may actually die some time later or be sterile;

(e) Treatment - The concentration of chemicals needed to flocculate the sump fluid for the laboratory examination is now utilized to predict a treatment for clarification of the sump fluid in the field. This is then followed by a treatment of the sump in the field that is specific to the type of poison most probably causing the toxicity. Another paper will be given at this symposium setting forth various precedures for field detoxification of poisonous sumps.

SUMMARY

Companies, as well as Government agencies, should work together to insure that:

(a) Methods of recycling waste fluids be developed such that the ideal situation of little or no waste water may eventually be approached;

(b) The toxicity of all the chemicals used be evaluated in relation to their effect on the environment;

(c) Alternative chemicals be developed which are less toxic than those currently used;

(d) Methods of detoxifying effluents be evaluated such that each situation can be effectively and cheaply dealt with;

(e) Samples of all effluents, whether they have been treated or not, be finally checked for toxicity prior to disposal by using some species of live animal;

(f) Research and Development be encouraged by the surveillance arm of the Government such that there is an incentive gain to research. This could be managed via tax relief, but should result in improved practices (i.e., reduction in volume of waste water and/or development of more effective, less toxic chemicals).

REFERENCES

1. *Diagnosis and Improvement of Saline and Alkali Soils*, Agriculture Handbook No. 60, U.S. Department of Agriculture, U.S. Government Printing Office, Washington, D.C. (p. 70, particularly).

2. *Standard Methods for the Examination of Water and Waste Water*, 13th Ed., 1971, American Public Health Association, 1015 Eighteenth Street, N.W., Washington, D.C. 20036.

DISCUSSION

MR. DENNIS G. WRIGHT (Environment Canada, Winnipeg, Manitoba, Canada): Could you outline the methods that you use in your trout check?

MR. SHAW: I would prefer to say, find a determination of water and sewage in *Standard Methods for the Examination of Water and Waste Water* (ref. 2). It is covered on page 568, if I remember correctly.

I used an alternative, as specified there. I do not use, generally speaking, 10 fish. There are reasons for it. I will go into that quite deeply with you if you wish.

You see, the point is that what you wish to do is find an indication. You are not concerned, by and large, with the TLM's and your threshold limits and this kind of thing. I generally do not head this way.

MR. DONALD L. WHITFILL (Continental Oil Company, Ponca City, Oklahoma): With the exception of, say, biocides, do you feel that turbidity, pH, and conductivity tests could accomplish what you are shooting for there?

MR. SHAW: Well, if you mean to tell you whether the material is toxic or not, no, definitely not. I am sorry.

MR. WHITFILL: This is what I was wondering about, because you pointed out quite frequently that, normally, turbidity would give you some idea about the bentonite; conductivity is going to give you some idea about the total dissolved salts that are in there; and you pointed out that pH by itself is not an indication, but that pH and conductivity together will give you quite a bit of information as far as salt values.

MR. SHAW: You could, for example, have a material that is nonionic in nature and still exceedingly poisonous. If sugar were poisonous, that would be an example, since it is a material that is nonionic in nature.

So you cannot really correlate your toxicity to an ionic structure, either conductivity or otherwise.

MR. WHITFILL: I feel this is quite true in most cases. But most of the time we know what materials we are putting into a mud system.

MR. SHAW: Most of the time you think you know. I mean, I have had several cases of sumps that were toxic and people say, "Oh, no, we did not put any chemicals in." Then you begin checking and you find out they used rig-wash chemicals that are extremely toxic.

MR. WHITFILL: Right. So you have to make the assumption that you do know what you put in, for this sort of test.

MR. SHAW: Well, as you know, there are a lot of commercial materials on the market that are patented or trade secret mixtures, and you may know a major ingredient but very often you do not know the minor ingredients, and they can often be the ones that are toxic.

MR. WHITFILL: Did I understand that you had 100 milligrams per liter chloride maximum?

MR. SHAW: No. A thousand, I believe, was the rough rule of thumb, but this is after the detoxification step and not prior to it.

SOME BIOLOGICAL IMPACTS ON THE AQUATIC ENVIRONMENT BY GEOTHERMAL ENERGY DEVELOPMENT

Max Katz, Ph.D.*

It seems that I was asked to give this talk because someone spotted my name as chairman of the Biological Impacts Committee at a recent workshop on Environmental Aspects of Geothermal Resources Development (ref. 1).

I would like you to know that I accepted the chairmanship of that committee only after I was assured that I did not have to prepare a paper, and did not have to give a talk. Nevertheless, here I am. I certainly do not wish to assume the position of an expert on the environmental impacts of geothermal development. I do not know anything special about the biological aspects of geothermal development on aquatic organisms because my limited experience indicates that the environmental problems of geothermal development are not unique. I do not want people to think that geothermal energy development is opening a new bag of worms. It is not.

In fact, the only thing that is unique so far about the environmental impacts of geothermal development, as far as I am concerned, is the nice places that you get to work, and the rather spectacular views of steam escaping from the various geological structures and artificial devices that you get to see. Instead of the typical soiled industrial development, you do your work in rather beautiful scenic areas and the unique environmental hazard that I have found is well-nourished rattlesnakes--which is a worthwhile trade-off if you are a rattlesnake fancier.

But to get back to the biological impacts of geothermal development, I want you to take note that our Committee on Biological Impacts at Asilomar seemed to be the most vocal of all of the groups that participated in that workshop, because we came up with 21 real and imagined biological impacts, while, for example, the Water Quality Committee came up with six problems, and the Air Quality group only four problems. There was, of course, considerable overlap in problems and our committee listed all of the problems included in the Water Quality Section.

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Now of course you in the working world, as contrasted to the academic or regulatory world, may feel that many if not most of the problems that my committee listed among the biological impacts (ref. 1) were imaginary or that we were making mountains out of molehills. Most of the industrial people who participated in the workshop took this view in regard to our list of biological impacts. They may not have been right, but they were very sincere and vocal in their objections. On the other hand, the conservationists accused our committee of overlooking and underplaying the true hazards. Our committee felt, however, that if someone of even modest competency thought that there was a problem in regard to geothermal development, then it was a genuine problem, and should be so listed and considered. This is actually a realistic approach because I, and I am sure others of you, have found out that if a group of dedicated and aroused environmentalists believe that a problem exists, then they can create a climate of public opinion that has to be answered. If a segment of the public believes that drilling will cause earthquakes or will reactivate the dinosaurs, then all earthquakes therefore are a result of drilling, and we have to prepare for the dinosaurs, unless you can prove otherwise. Environmentalists and regulatory agencies are able to, and have not been at all reluctant to stop projects for reasons that have little or no scientific and technical validity--nonsense and irrationality are real factors in the environmental business and we had better not forget it--and it is mandatory that the energy developers come up with convincing answers to their charges. This is part of the business.

Obviously, I do not have the time in this talk to go over all of the 21 biological impacts proposed by my committee at Ansilomar, which is fine, because I am not prepared to discuss on a professional level those problems other than the aquatic problems. And some of the aquatic problems are not real enough in my opinion to be worthy of using this limited time for discussion. When we get down to the potential aquatic problems of enough timely importance or interest to be worth discussing, we find that these problems are often not unique to geothermal development, but are common to other industries and land uses. They have been studied, discussed, and fairly well understood and were under a degree of control well before geothermal energy and its development became popular areas of concern and discussion. Some of these concerns--for example, thermal discharges--are already under many sorts of strict controls at the Federal and State levels. But I would like to see how State and Federal legislation can compel a fumarole that has been discharging hot water for a hundred years or more in the bottom of a stream to cool down and start producing cool water.

Thermal Discharges

One of the first biological impacts considered by our committee was the thermal effect of liquids discharged from the power site on organisms in the receiving waters. The effects of thermal discharges from industrial operations, thermonuclear and fossil fuel power plants, have been documented in a voluminous literature. Robert C. Axtmann, in a recent paper in Science (ref. 2), has documented thermal discharges as one of the major environmental impacts of the Waireki Geothermal Power Plant on the Waikato River in New Zealand. Incidentally, for those of you in the regulatory agencies who would like to have a listing of most of the undesirable effects of geothermal development upon which to build a regulatory structure, I would suggest Axtmann as a good reference.

In my experience, the thermal impacts at The Geysers were from fumaroles, hot springs, and warm soil in the bed of Big Sulphur Creek. Big Sulphur Creek drains most of the area in The Geysers development. The thermal effects of these springs are evident primarily during the low-flow periods of the summer and early fall, at which time the radiant energy addition from the sun is substantial. Water temperatures were too high for trout, while suckers and minnow species that preferred higher water temperatures were the predominant fish species and were present in large numbers.

In developments in which significant amounts of warm water are involved, the liquid discharged into surface waters may have to be cooled to meet the water quality criteria of the State and Federal agencies.

Dissolved Substances

Another biological impact regarded as important by most members of our workshop was the toxic effect (both lethal and sublethal) on aquatic organisms of the dissolved mineral substances in condensates. These condensates may vary in different developments from quite soft water to supersaturated brines that precipitate as salts as they cool. These salts can affect water quality considerably by changing the salinity, affecting the pH, and by the toxic metals which might be present.

Axtmann (ref. 2) presents a table of the chemical discharges to the Waikato River by the Waireki Geothermal Power Plant. It is presented here as table 1.

Table 1. Chemical discharges to the Waikato River (ref. 2)

Constituent	Increment in River Concentration (ppm)	Constituent	Increment in River Concentration (ppm)
B	0.27	Cl	29.8
Li	0.13	Br	0.055
Na	12	I	0.0047
K	1.9	NH_4^+	0.014
Rb	0.029	SO_4	0.24
Cs	0.026	As	0.039
Mg	4.7 x 10	Hg	1.5×10^{-6}
Ca	0.17	Silica	6.3
F	0.077		

Axtmann (ref. 2) quotes a source that states that the geothermal plant discharge supplies 75 percent of the arsenic input into the stream and believes that a sizeable contribution of mercury to the river system is supplied by the plant. Let me emphasize, Axtmann does not state that there are adverse biological effects due to mercury and arsenic. Mercury ore deposits are frequently found in association with hot springs (ref. 3). In fact, abandoned mercury mines are characteristic of the area surrounding The Geysers. For example, the metropolis of Mercuryville, population 2, is a landmark on the road between Santa Rosa, California, and The Geysers. Again, let me emphasize, we often find geothermal sources where we find mercury ore deposits. Geothermal development does not produce mercury or utilize mercury; it is already there.

The presence of substances such as arsenic and mercury, regarded to be deleterious to aquatic organisms, is of interest, but should not be a serious problem unless someone wishes to make it so.

Even if an agency should decide the mercury or arsenic content is unduly high in fish residing in a stream or receiving water, one could simply classify the stream or lake as a trophy fish stream. One then would be allowed to fish, but would not be allowed to keep the fish taken. With the reduced mortality and the reduced patronage of the "meat" fishermen, the stream would become a habitat for large fish and would be more popular than before and would be regarded as a superior recreational asset. The management of streams and lakes as trophy fish sources is an accepted management practice in Washington State and other places.

pH Changes or Acid Water

Although our panel believed that there was only a slight chance of this occurrence, we discussed the possibility of acid rain as a result of geothermal development. The better chemists on my committee felt that it is possible that the H_2S that is often part of the vapors in thermal areas could oxidize to SO_3, and then would fall as H_2SO_4 in the rain. This precipitation might possibly lend to the acidification of lakes and streams, especially if the streams were slightly buffered, as are many of the lakes and streams in our coastal mountains. Acidification of lakes and streams is documented by Brosset (ref. 4) in Sweden, and by Beamish and Harvey (ref. 5) in Canada. There is no documentation that this has happened as a result of geothermal activity. The Canadian experience is a result of smelter operations in Ontario, and is not due to a geothermal development.

Effects of Drilling Substances on Aquatic Organisms

The toxic effects of drilling substances on aquatic organisms is a problem that was taken quite seriously by members of my panel, and is obviously being taken quite seriously by the present meetings. None of the speakers on the present program were on my workshop panel at Ansilomar and none of my panel, to my knowledge, presumes to an expertise that is equal to that of the speakers at this meeting. Our panel was concerned with the problem of the safe disposal of drilling muds and insuring that they were not discharged advertently or inadvertently into the waterways. They presented some recommended approaches to solving the environmental problems of drilling muds. These recommendations were (ref. 1):

1) As part of the planning for the exploration and development of the field, provisions should be made for the safe disposal and removal of drilling muds.
2) During the operation, care should be made to insure that the waste drilling products are retained and stored in the areas cleared for the drilling operation, or in an area where they can be watched and accounted for and where the chance of their being discharged into a water supply is slight or impossible.
3) Many of the drilling muds have components that are toxic to aquatic organisms. The composition of the drilling muds should be known to some responsible person so that the toxicity can be predicted. It should be possible perhaps to select from several drilling preparations one or two nontoxic muds that could be used to do the job in an area where there are many productive lakes and streams.
4) In areas in which there are few lakes and streams and where accidental discharges will have minimum aquatic effects, the choice of drilling substances qould be based on mechanical efficiency and cost.

A laboratory research effort could be directed to determine the component and components toxic to aquatic organisms of interest. Changes in formulation and substitution of less toxic components might be made to reduce the toxicity and to confine effects of physical stresses, e.g., siltation and sedimentation.

Reinjection Waters

Another problem that was of real or potential significance was the effect of reinjected water that might escape either by accident or by poor engineering into the surface water and affect aquatic organisms.

It is a policy, I understand, to reinject moisture back into the wells for good technical reasons. If the waste waters were injected into formations from which they would not escape into surface water supplies, then obviously, there would not be a biological problem. If the reinjected waters were pumped into a formation from which they would escape to surface water supplies, a problem of water quality affecting aquatic organisms might occur. Our group felt that this problem was quite readily soluble by good engineering practices, and should not be a problem in any project that utilizes such practices.

Erosion

The biological impacts of sedimentation arising from the erosion from surfaces disturbed by the explorations and the geothermal development is by far the most potentially disturbing of the problems that I have observed. When roads and trails are built into previously undisturbed areas, when the ground is cleared and leveled, or when the land is hilly or mountainous and is subjected to heavy seasonal rains, we have a potential and a probability of soil washing into the streams and causing problems which vary all the way from the esthetic to perhaps serious local disturbances of the stream bottom.

In my limited experience, the biological impact of soil erosion is a major aquatic impact of geothermal development. Of course, my opinion was formulated at The Geysers area, which is in the California coastal mountains, and is characterized by a wet winter season and a dry summer season. The erosion problem is compounded there by a serious overgrazing situation.

Erosion and its biological effects, as seen at The Geysers, would not be as great a problem in more level terrain or in a drier climate or a less agriculturally abused area. Fortunately, or unfortunately--depending on the side of the fence you are on--the trubidity resulting from erosion is quite visible in a stream, and is readily measurable. A few parts per million of turbidity is readily obvious, and is a temptation to enthusiasts to extrapolate widely all sorts of biological impacts--real and imaginary. And do not forget the general public usually chooses to select the wildest imaginary impacts upon which to base its environmental activity.

I wish to make it clear that even at The Geysers, which has the conditions conducive to erosion damage, that siltation due to erosion is not a serious environmental impact. The impact there is the hot springs and warmed ground that increase water temperatures in the vicinity of the stream.

Endangered Species

The last biological impact, and one that really concerns me, is the effect on endangered species. This concerns me because I am an aquatic biologist and I am an aquatic biologist because I like aquatic organisms and I think that they are wonderful creatures and should be preserved. We can get into a philosophical discussion, but I believe that the presence of a pond with an unusual array of bugs and fish contributes to my conception of the quality of life and is as important to man as a tank full of gasoline is for an automobile or the power to run a T.V. set. And if we have to spend a few thousand dollars more or spend an hour more of planning to preserve a little swamp that is one of the few remaining homes of a rare organism, we should do so. I still think that life should be worth living and interesting organisms are a part of that good life.

Thermal areas are marked often by warm ponds, hot springs, or other unusual and unique environments which, over the centuries, develop an interesting complex of animals and plants. These areas are often quite small and few in number and quite unknown, except perhaps to the biologists in the closest college or State University. These habitats can easily be destroyed by a few passes of a bulldozer blade. But they need not be destroyed. They are local treasures and should be respected.

Destroying the small ecological treasure is often pure vandalism and is not good development practice.

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DISCUSSION

MR. DONALD W. HECKER (Union Oil Company of California, Los Angeles, California): Max, you mentioned the Science paper which goes into the environmental effects of condensate and discharges into streams. I think we should mention here that this particular problem is nonexistent in the United States because the U.S. geothermal industry has made a standard practice of the reinjection of all of the condensates from our geothermal operations.

DR. KATZ: Good.

DISCUSSION

CHAIRMAN GIAM: Earlier in the day there were a few questions (during individual lectures) that we could not answer due to lack of time. If the questioners are still here, I think we can entertain those questions.

DR. CHARLES F. JELINEK (Food & Drug Administration, Washington, D.C.): I wanted to ask one question. I do not know if anyone has the answer that would help put into perspective this question about pentachlorophenol and whether it might form dioxins under conditions in oil fields. Does anyone here know how many pounds or hundreds of thousands of pounds of chlorinated phenols are used in oil field operations? I think that would do a lot to tell us whether this might really be a problem or not.

MR. HARRY L. HARRISON (A C Drilling Specialties, Odessa, Texas): I am not at all an expert on chlorinated phenols, but these materials are used as preservatives in the sack mud. When it is used in the field, it is used in the sack in concentrations of less than one percent.

When you put the chlorinated phenols in the mud system, they go way down and, consequently, in the overall system the level is very low. I have no numbers on this, but it would be low to begin with.

CHAIRMAN GIAM: Would you think it is in the parts per billion range?

MR. HARRISON: No, I would not go quite that low.

I understand these compounds are quite susceptible to calcium and precipitate. Calcium is a problem in any drilling system, at least those in West Texas and Southeastern New Mexico; and it is something that we have not gone into here. We always are drilling into the calcium deposits and have calcium counts in mud that run up to 5,000 to 6,000 parts per million.

MR. WALTER J. WEISS (Texaco Incorporated, Bellair, Texas): The chlorinated phenols are used to preserve the gum type of fluids. They are usually used at about 300 parts per million, and that level is recommended in the formulation.

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CHAIRMAN GIAM: (Comments refer to the possibility of a dioxin being produced in drilling fluids or muds during drilling operations at high temperatures.) I am suggesting that a well resembles a reaction pot. For example, let us find out if the ingredients such as phenol and sodium hydroxide for salt (pentachlorophenol) formation are there. If these ingredients are there--in the parts per million range--I would like you to consider the following: First, you should do some research and find out what the yield under these conditions is. If the yield is 50 percent or 30 percent, you are still in the parts per million range of this dioxin. If indeed that is true, then the next question you have to ask yourself is how much of this mud with parts per million you are dumping? Where are you dumping the mud? What are the species that are eating it? And will these species that are eating the phenols, the dioxin, be ultimately consumed by man?

If answers to these questions are all yes, then I strongly suggest that you look into dioxin formation very seriously because you may have a problem that at one time 245-T was not acceptable. I believe one of the problems of 245-T was the fact that toxic benzodioxin was present in parts per million. Please remember, I said all the ifs. I am not suggesting that dioxin is present. I am sure all of you would want to make sure that dioxin is not present. So I hope I made my statement very clear. I do not know whether your question has been answered, Dr. Jelinek.

DR. JELINEK: No. Actually, what I wanted to know is how many hundreds of thousands of pounds of pentachlorophenol are used in the whole United States in well operations, to help put this in the proper context.

MR. FRANK J. SHELL (Phillips Petroleum Company, Bartlesville, Oklahoma): I think it depends partly on where the material is used rather than how much is used. We do not use pentachlorophenol in a hot part of the hole where a dioxin reaction would take place. This material is always used in the upper part of the hole. We have no reason to use it in the lower part of the hole and so we do not. We forget sometimes that the Lord made this universe, and He protects us even if we are not wise enough ourselves. And I think He has built in certain safeguards, like not letting man use a material like that where it would get him in trouble.

CHAIRMAN GIAM: Probably, by alerting people like us to watch over ourselves. That is one possibility.

DR. KATZ: The pentachlorophenol has been used by the Japanese as part of their pond culture of fish. I do not remember exactly the procedure, but I think the pentachlorophenol is introduced to kill the algae. After a couple of days, the pentachlorophenol breaks down in the sunlight. The Japanese then planted carp and away they would go, and they would harvest and market them when they got large enough. This is apparently a fairly well-accepted procedure there. Whether it is good or bad, who knows. It is better than dying of starvation, but it shows that pentachlorophenol and fish can get along if used correctly.

Another point I would like to bring up. All the time during this meeting you talked about the 13th Edition of the American Public Health Association in regard to the toxicity bioassay methods. I am not saying it is an injustice, but I would like to call your attention to the fact that these toxicity bioassay methods were developed by Dr. Peter Doudoroff. Some of you people may have it in your company's library--it is a Hart, Doudoroff, and Greenbank book that came out in 1943 or 1944. Pete Doudoroff headed the committee, in about 1950, of the Water Pollution Control Federation group that set up the toxicity bioassay methods used today. These procedures have been used again and again under many names, and Pete has been responsible for, you might say, nursemaiding this baby of his into the Standard Methods. To his great horror and disgust, everybody uses them incorrectly, but then that is not Pete's fault.

MR. J. P. SIMPSON (Baroid Division, N L Industries, Inc., Houston, Texas): I do not have an exact figure to give you on tonnage or poundage, but it is more in the range of poundage.

I would perhaps put it in perspective, though, by saying one mud out of a thousand might use pentachlorophenol and it might be closer to one in 10,000.

CHAIRMAN GIAM: Well, one good point, perhaps, that came out of this morning's off-the-cuff remark was I was talking with a gentleman from Dresser.

I had been informed that you do not have to use pentachlorophene if, indeed, in that reaction they found dioxins. You could use, say, formaldehyde.

MR. GERALD A. SPECKEN (Wilson Mud Service, Limited, Edmonton, Alberta): For what it is worth, I believe that pentachlorophenol is one of those compounds that on a trout bioassay would kill in about a part per million range. You can treat fluids for land surface disposal so that they pass these kinds of bioassays. Perhaps the significant thing is whether soil bacteria will decompose them when spread to the land, and I think that applies to any drilling fluid compound. But if you can remove them from the fluid when you dispose of the fluid, why can they not be used? What is the difference?

CHAIRMAN GIAM: If there are no more questions, I would like to thank all of you for your patience. I would like to thank Dr. Fisher.

23 May 1975

Session III:

ENVIRONMENTAL IMPACT OF THE BYPRODUCTS OF WELL DRILLING

Pat M. Wennekens, Ph.D.*
Chairman

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*Oceanographer, Alaska Department of Fish and Game, Anchorage, Alaska.

SESSION INTRODUCTION

Pat M. Wennekens,
Session Chairman

This morning's session has proved to be a very interesting session. Now that we know or we suspect what some of the waste material might be that is introduced into drilling fluid, the question becomes, "What do you do with such fluids once you do not want them anymore, and how do you handle them?"

The papers that are going to be presented will address themselves to this very germane problem.

We are faced with this very problem in Alaska, as in any place else. One of the main features that I think needs to be really improved upon; we must do much better planning for it. In many instances we do not want the waste released into a certain place nor do we want a waste treated in a certain way; but the problem remains--it has to be put somewhere. Unless we treat the problem as a total package--a total problem of waste handling--the problems of control handling, the method of disposal, and proper siting of disposal areas become a very crucial portion of the environmental planning and programs for this material.

My strong recommendation again is that we must look at a total package.

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THE HANDLING AND TREATING OF WATER-BASED DRILLING MUDS

Robert B. Allred*

Abstract

In the process of drilling most wells, a thixotropic colloidal suspension with water as the continuous phase is used to remove cuttings from the bore hole. This suspension is continually circulated during drilling operations from surface tanks down the drill pipe, out the nozzles of the bit, and back to the surface in the annular space between the drill pipe and the casing or open hole.

At the surface the unwanted solids, gases, and liquids are removed from the drilling fluid with specialized equipment. Discharged solid and liquid materials are either stored in holding tanks or reserve pits. Gases are properly disposed of at the well site. Contaminants and physical property defects are treated with various chemicals so that the drilling fluid is in suitable condition to make another trip down the hole.

Under normal conditions, drilling fluids are free from toxic properties, and spillage on personnel results in only momentary inconvenience. Proper washing of the derrick floor and walkways and other regular good housekeeping practices are the only precautions necessary in handling the drilling fluid. When high pH drilling fluids are used or toxic contaminants are encountered, special procedures are followed to insure the safety of personnel and the protection of the environment.

The advent of rotary drilling brought about the use of clay and water as a drilling fluid as early as the Lucas well at Spindletop in 1901 (ref. 1). Over the years, drilling fluid has developed from muddy water into a thixotropic colloidal suspension capable of removing cuttings from the bore hole, cooling and lubricating the drill pipe and bit, holding back formation pressures, and increasing penetration rate (ref. 2).

It is worthwhile to consider the nucleus of the colloidal suspension,

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a hydratable clay (in most cases a Wyoming sodium bentonite), which produces the property of thixotropy. Thixotropy is the property enabling certain colloidal gels to liquify when agitated and then to return to the jelly-like form when at rest. The drilling fluid is pumped down the drill pipe and sprayed out the bit nozzles, spearheading the grinding action of the bit. On its return to the surface, the velocity of the fluid is less than on the trip down the drill pipe, mainly due to the larger size of the annulus, the space between the drill pipe and the casing or open hole. The reduced velocity allows the formation of the colloidal gels, which suspend the cuttings produced by the bit and carry them to the surface. The gels are more intense when the fluid is in a static condition; therefore, if pumping is discontinued, the cuttings will remain in suspension and not fall to the bottom of the bore hole. In some wells (in order to overcome formation pressures) barite, barium sulfate, is added to the drilling fluid so that a density of up to 20 lbs/gal may be obtained. The barite is also suspended by the clay particles.

A drilling fluid contains solids, liquids, and sometimes gases. There are two types of solids with a variation of sizes: the wanted ones - colloidal solids, clays (0-2 microns) and weight material (barites) (1-60 microns); and the unwanted ones - drilled solids, silts (2-74 microns), sands (>74 microns), limestones, anhydrites, and other contaminants (ref. 3). The continuous liquid phase is water, which varies from fresh to saturated salt. In nonrestrictive areas, some drilling fluids carry 2 to 10 percent emulsified oil, diesel, or crude. In some wells, unwanted gases (some contain hydrocarbons or hydrogen sulfide) may be defused into the mud system. See figure 1 for an overview of the circulating system.

When the drilling fluid comes to the surface, the unwanted constituents are removed by different methods of separation. The gas (hydrocarbon) not entrained in the drilling fluid is removed by flowing all of the mud through a mud-gas separator inserted in the flowline between the casing annulus and the screening machine. The mud-gas separator, as shown in figure 2, is usually a large-diameter pipe with interior baffles to slow down the mud stream. This permits the gas to go out the top and the mud

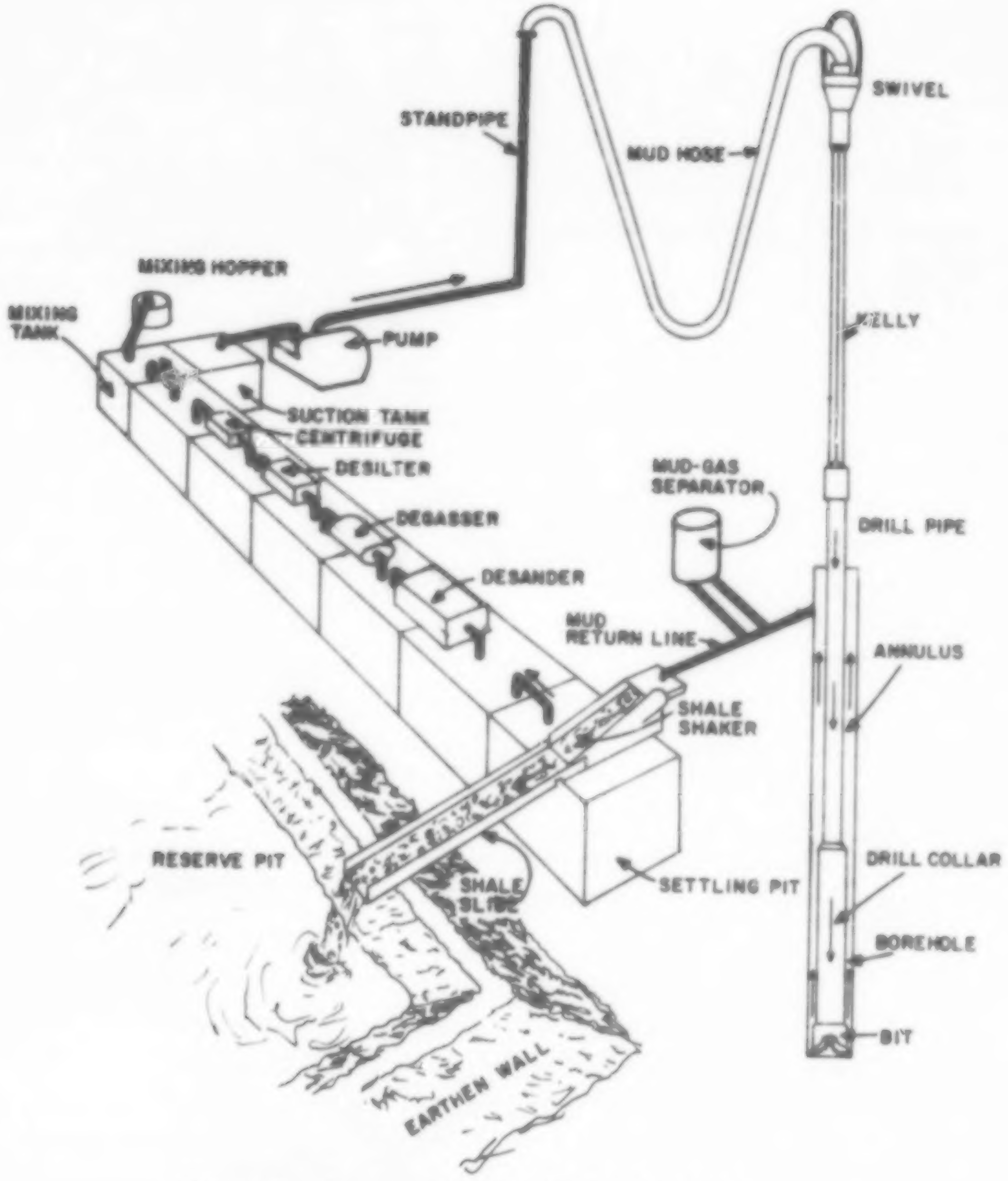

SWIVEL
STANDPIPE
MUD HOSE
MIXING HOPPER
MIXING TANK
PUMP
KELLY
SUCTION TANK
CENTRIFUGE
DESILTER
MUD-GAS SEPARATOR
DRILL PIPE
DEGASSER
DESANDER
MUD RETURN LINE
ANNULUS
SHALE SHAKER
RESERVE PIT
DRILL COLLAR
SHALE SLIDE
SETTLING PIT
BOREHOLE
BIT
EARTHEN WALL

Figure 1. Components of a fluid circulating system.

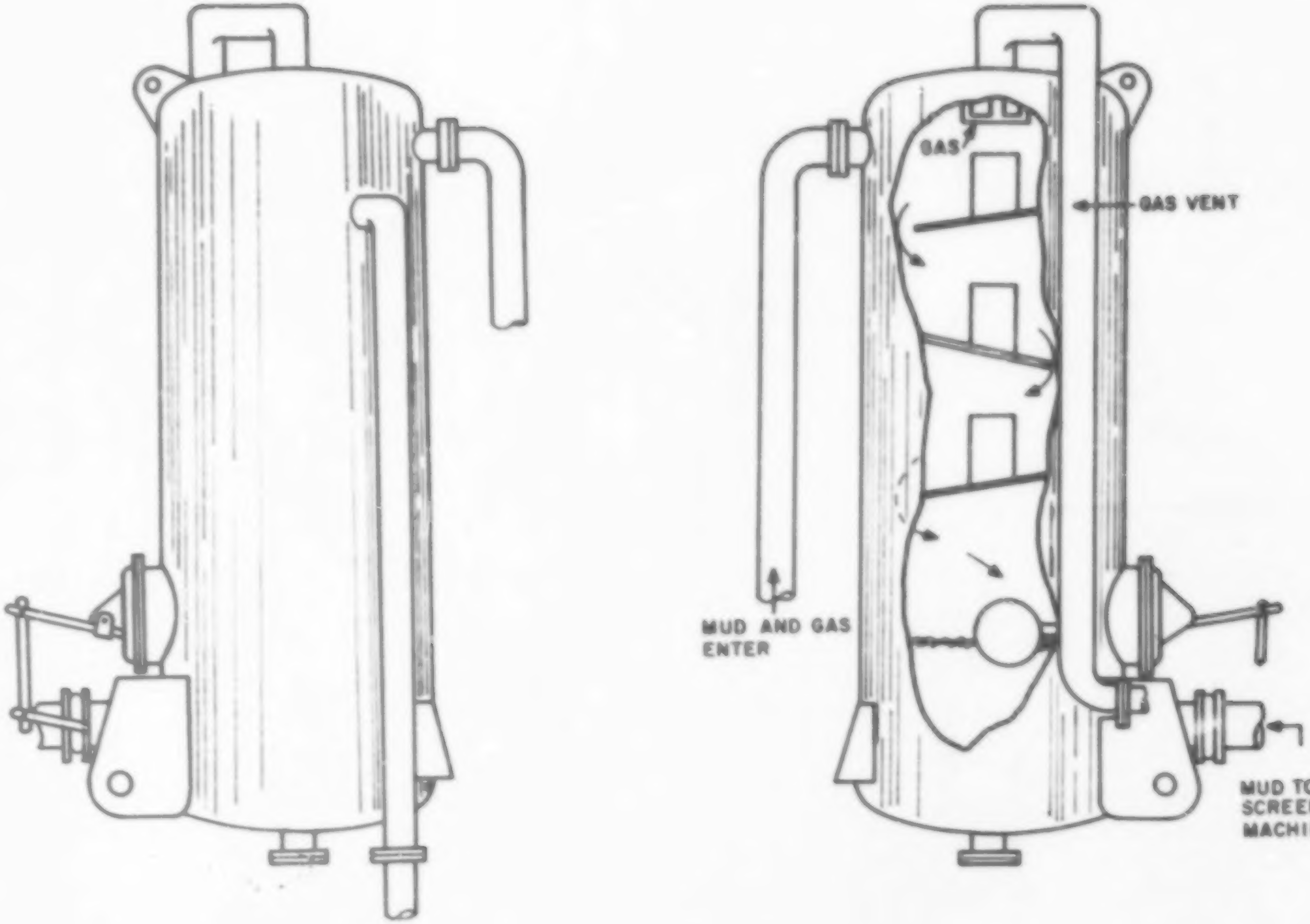

GAS
GAS VENT
MUD AND GAS ENTER
MUD TO SCREENING MACHINE

Figure 2. Mud-gas separator.

to go out the bottom. The gas is then piped from the top of the separator and safely vented away from the rig to a flare pit where it may be burned if necessary.

A recent addition to the "Notice of Lessees and Operators of Federal Oil and Gas Leases in the Outer Continental Shelf, Gulf of Mexico Area on Hydrogen Sulfide in Drilling Operations" states that: "Drilling mud containing H_2S gas shall be degassed at the optimum location for the particular rig configuration employed. The gases so removed shall be piped into a closed flare system and burned at a suitable remote stack." It also presents new orders on the handling of gas that is circulated to the surface when killing a well. The order states that: "The disposal of H_2S and other gases shall be through pressured or atmospheric mud-gas separator equipment, depending on volume and pressure of H_2S gas. The equipment shall be designed to recover drilling mud and to vent to the atmosphere and burn the gases separated." From the mud-gas separator the drilling fluid goes to the screening machine, thus beginning solids separation.

Vibrating screening machines come in many different sizes and configurations with any number of screens. A triple-deck screening machine is shown in figure 3. Most of the modern machines shake or vibrate in some manner and use sieves so that the liquid will go through the sieves and into the sand trap. The sieve sizes vary from 10 to 80 mesh. Thus, it is possible to remove all particles greater than 178 microns depending on the sieve size. The solids will remain on the screens and be transported off the screens and out of the mud system into the discharge pit. The screens are horizontal, sloped, stacked, or a combination of these. The screening machines are planned so that the greatest amount of solids (depending upon the particle size and amount of solids plus the circulating rate) will be removed from the mud stream. Although efforts are made to lessen it, some water is removed from the mud stream along with the solids by the screening machines. Vibrating the screens helps remove the water from the solids. Backing fine screens with coarse screens, so that a wicking effect can take place, also removes water from the solids.

The mud falls through the screens and into settling tanks. Settling tanks or sand traps are, as the name implies, places where the fluid is

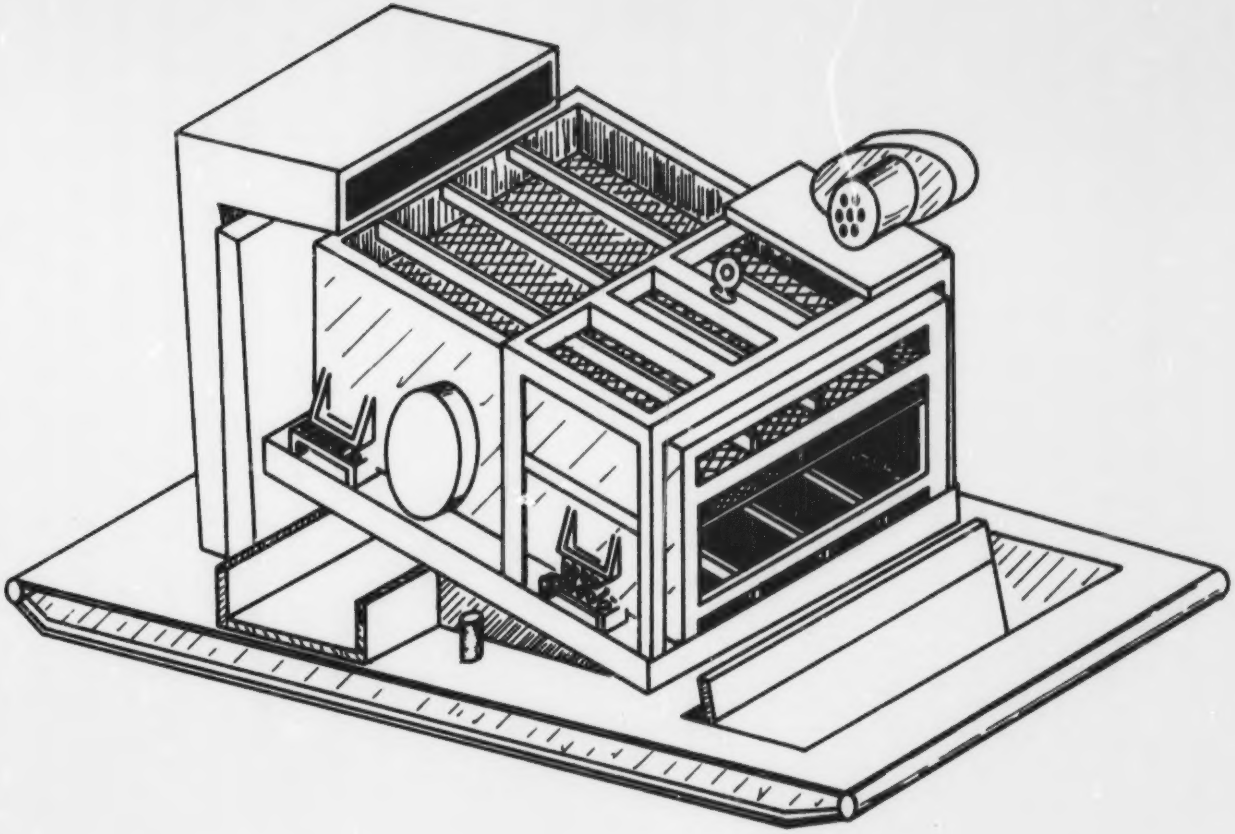


Figure 3. Screening machine.

allowed to be in a near static or static condition so that large and/or heavy particles will have an opportunity to drop out of the drilling fluid. The size of the tanks depends on available space and equipment. Sand traps in the active system should have sloping bottoms so that they may be easily cleaned (ref. 4).

After leaving the sand traps, the drilling fluid is pumped into the degassing or desanding and desilting compartments. If the drilling fluid does contain entrained gas (hydrocarbon), it goes through a degasser prior to entering the desander or desilter. There are many types of degassers, all of which spread the mud as thinly as possible on some surface permitting the entrained gas to migrate out of the mud. The gas is removed by a vacuum pump or other depressuring device and vented away from the drilling rig. One such degasser is shown in figure 4.

Desanding and desilting are done by the use of hydrocyclones, the type of solid removed depending upon the size of hydrocyclone used. Desanders are usually 6-inch to 12-inch cyclones that can remove particle sizes of 25 microns and larger. Desilters are usually 4-inch cyclones that can remove particle sizes of 15 microns and larger. The number of cones used should be dependent upon the maximum volume of mud circulated during the drilling of the well.

In a hydrocyclone as illustrated in figure 5, pressure energy is converted into centrifugal force by tangentially feeding the drilling fluid into a conical vessel. The centrifugal forces developed multiply the settling velocity of the larger suspended solids, driving them outward toward the conical wall and downward to the solids discharge point at the bottom of the cone and out to the discharge pit (ref. 5). Each solid particle is coated by water as it leaves the bottom of the hydrocyclone. The water phase and smaller particles of the mud, being lighter, move inwardly and upwardly as a spiraling vortex to be discharged at the top of the cone and reenter the mud system. After being desilted, the drilling fluid can now be centrifuged.

There are different types of centrifuges, but they basically produce the same results and operate from the same principles of separation (ref. 6). They are capable of separating particle sizes from 2 to 9 microns from the larger particle sizes. A decanting centrifuge is shown in figure 6.

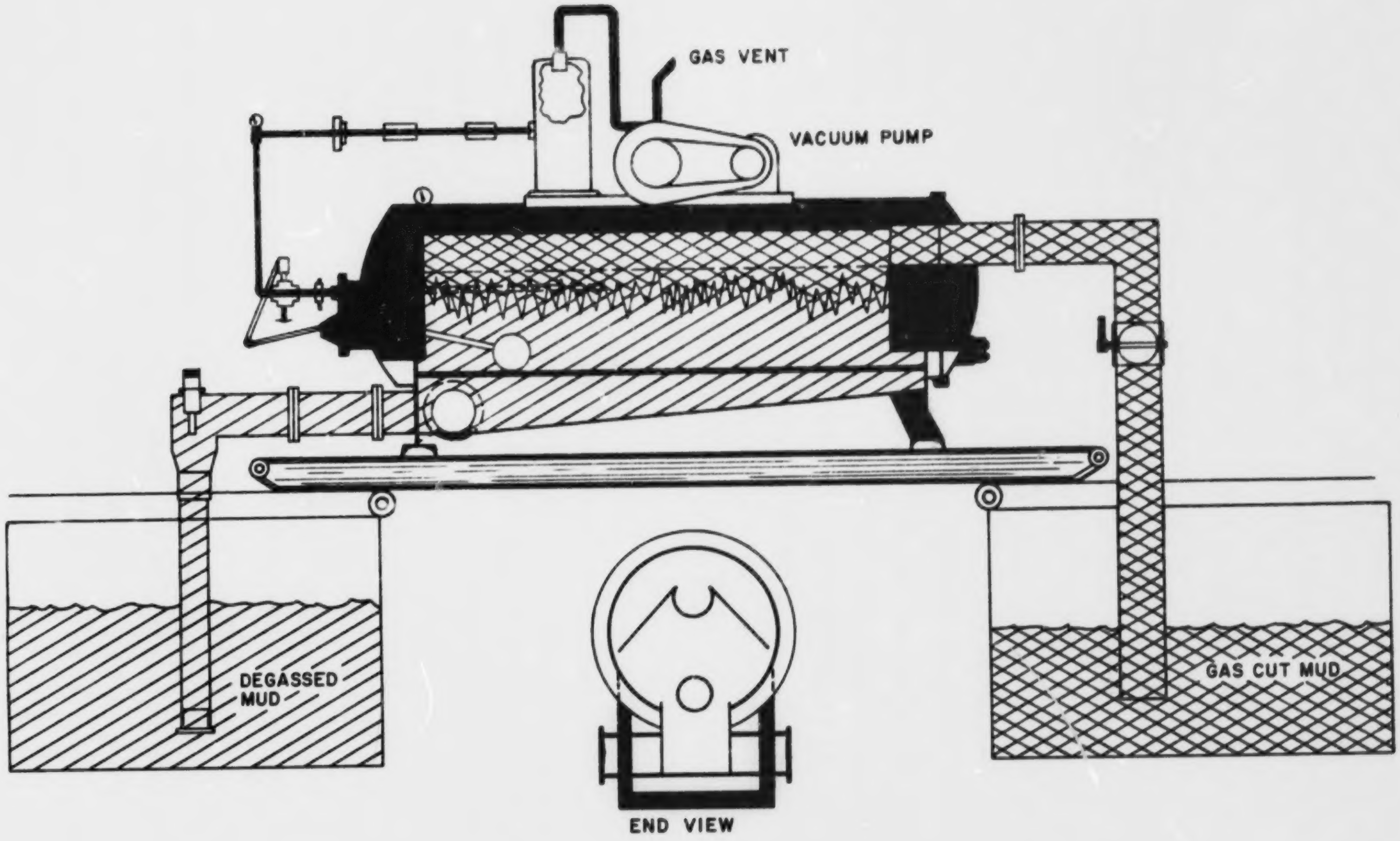

GAS VENT
VACUUM PUMP
DEGASSED MUD
GAS CUT MUD
END VIEW

Figure 4. Degasser.

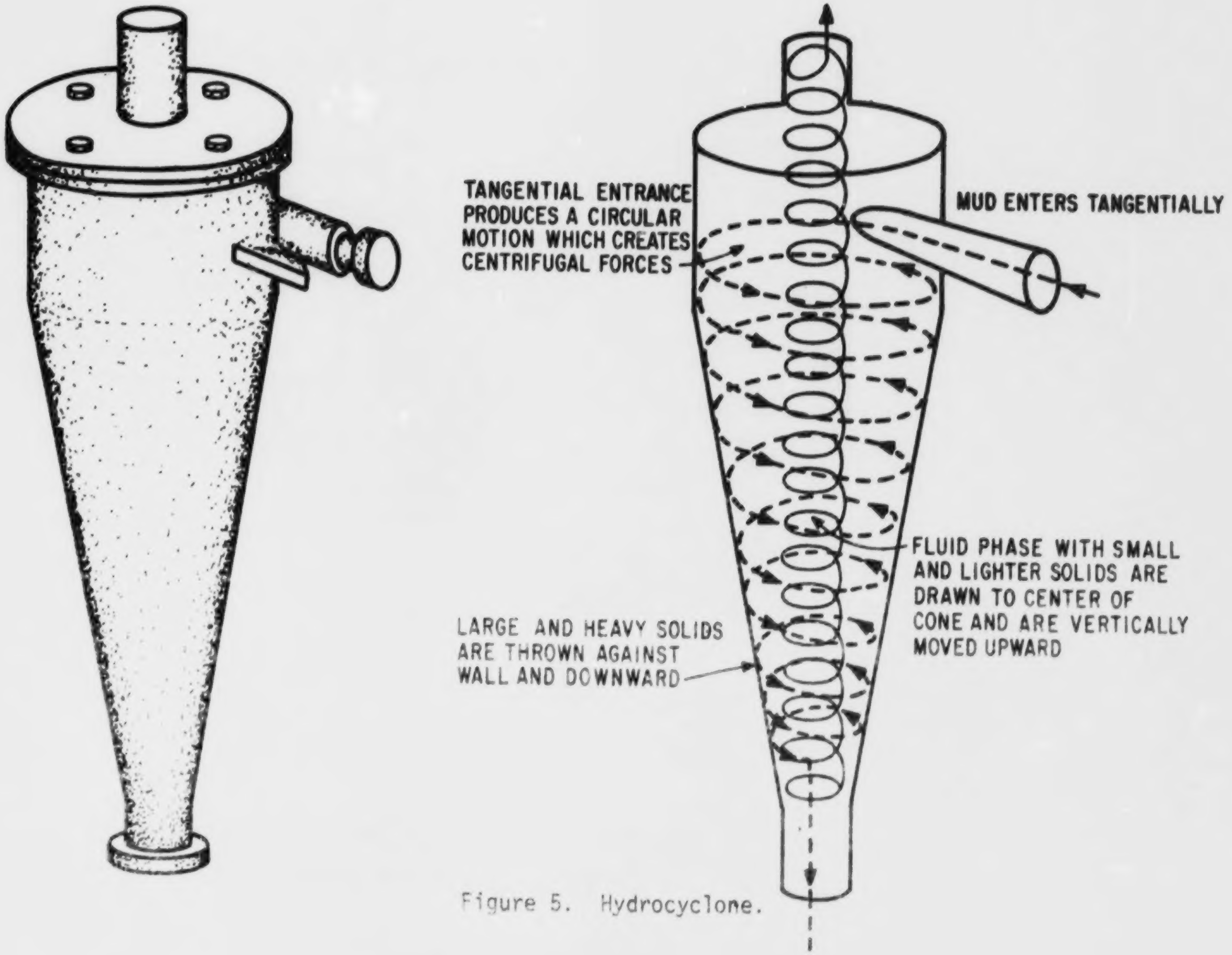
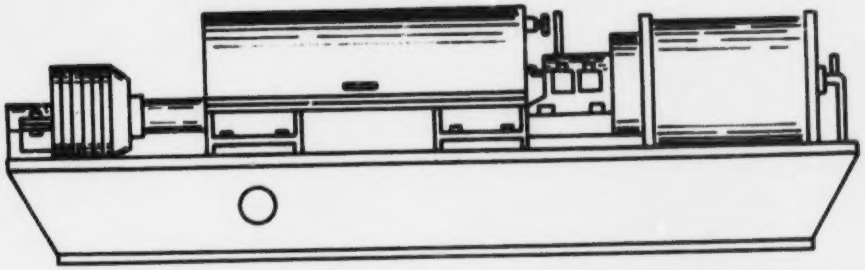

TANGENTIAL ENTRANCE PRODUCES A CIRCULAR MOTION WHICH CREATES CENTRIFUGAL FORCES
MUD ENTERS TANGENTIALLY
FLUID PHASE WITH SMALL AND LIGHTER SOLIDS ARE DRAWN TO CENTER OF CONE AND ARE VERTICALLY MOVED UPWARD
LARGE AND HEAVY SOLIDS ARE THROWN AGAINST WALL AND DOWNWARD

Figure 5. Hydrocyclone.



DECANTING CENTRIFUGE

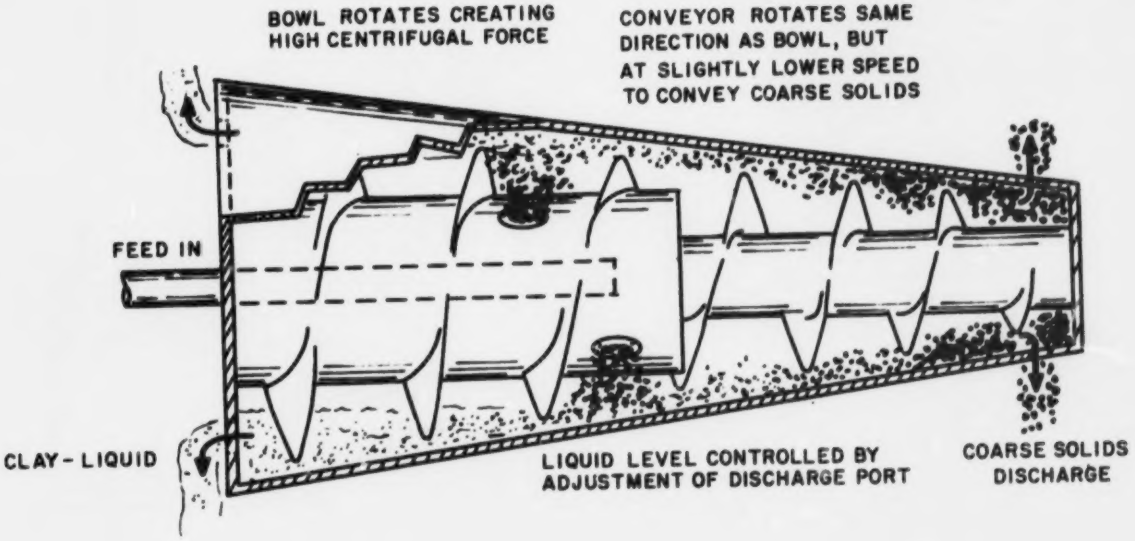

BOWL ROTATES CREATING HIGH CENTRIFUGAL FORCE
CONVEYOR ROTATES SAME DIRECTION AS BOWL, BUT AT SLIGHTLY LOWER SPEED TO CONVEY COARSE SOLIDS
FEED IN
CLAY-LIQUID
LIQUID LEVEL CONTROLLED BY ADJUSTMENT OF DISCHARGE PORT
COARSE SOLIDS DISCHARGE

Figure 6. Cross section of a decanting centrifuge.

Mud is diluted with water as it enters the centrifuge to reduce viscosity and allow efficient separation of solids. As the diluted slurry is rotated by the machine, G forces of 800 to 1,000 are produced, driving the larger and heavier particles to the outside of the bowl where they are conveyed to the coarse solids discharge. The fluid and smaller, lighter particles stay in the inside of the bowl and are conveyed to the liquid discharge. Depending upon which stream carries the desired solids or liquids, one is returned to the mud system while the other goes to the waste pit. If a high-density fluid is processed, the larger, heavier solids are mostly barite and they are returned to the active system, while the liquid phase containing viscosity-producing colloidal solids is discarded to the waste pit. However, in an unweighted polymer fluid, the liquid discharge carrying the expensive polymer is returned to the mud system while the solids, mostly drilled solids, are discarded. Centrifuging is the last stage of solids removal, so the drilling fluid then goes to the chemical treating tanks.

The drilling fluid is treated with chemicals so that viscosity, gel strengths, and density are of correct values. At this point, the aforementioned drilling fluid functions and efficient removal of solids and gases can be performed. Flocculating drilled solids with calcium compounds or polymers in particular mud types are also used to improve efficiency of solids removal (ref. 7). If poisonous hydrogen sulfide gas is encountered, it is chemically neutralized and not allowed to leave the mud as a gas. Water-base drilling fluids themselves are usually not harmful to humans (ref. 6). However, when the drilling fluid is being prepared or chemicals added for maintenance purposes, precautions are taken in the handling of concentrated compounds. Goggles, gloves, and breathing apparatus are used at the mixing hoppers. Neutralizing solutions are placed in strategic areas so that harmful effects from the chemicals can be avoided.

Once drilling fluids are mixed, only basic good housekeeping practices and precautions are necessary in handling the drilling fluid. The lubricating qualities of mud may cause the drilling floor and walk to become hazardous. Continuous washing of the areas where the mud is spilled insures safe passage. The use of high-alkalinity muds requires added flushing precautions and the use of neutralizing solutions by the crew.

Removed solids are usually diluted with water before they are dumped into the waste pit. If harmful chemicals such as high-alkaline compounds or oil are used in the drilling fluids, special handling of the removed cuttings is required.

Training is conducted at the wellsite on the proper handling of dangerous drilling fluids and their component parts.

Proper drilling fluid management requires great care in the mixing, handling, and use of the fluid components to protect the health and safety of the employee and to safeguard the environment.

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DISCUSSION

CHAIRMAN WENNEKENS: What do you do with this colloidal material? The colloidal material might be a carrier of a lot of the toxic fractions. And I was wondering if you had any thoughts on that.

MR. ALLRED: I will tell you what we do with it.

If we remove the colloidal material with a centrifuge, it is cut with water, and it goes to the reserve pit of the waste areas, where we throw it away. We remove it from the drilling fluid.

If it is, as I pointed out, a polymer or something that we want to keep, we keep it in the drilling fluid, because the drilling fluid is a colloidal suspension; we certainly need the colloidal solids that are in there. But sometimes in the process of removing some solids we have to remove those that we also would like to keep.

MR. GEORGE H. HOLLIDAY (Shell Oil Company, Houston, Texas): Dr. Wennekens, I was rather intrigued by a comment that was made by Dr. Fisher a couple of minutes ago about the work that you had done in Alaska in looking at the environment. And I wonder if you might permit me to ask what field evidence you have found of any environmental damage as a result of the drilling operations in the marine environment of Alaska?

CHAIRMAN WENNEKENS: I do not know if this is germane to answer this at this particular moment, but for those who are interested I will be glad to sit down at lunchtime and have a discussion about that. At this particular time, with the schedule we have, I do not think I can really respond on this. So if you could wait, I will.

MR. HOLLIDAY: Yes. Do you have any evidence?

CHAIRMAN WENNEKENS: Evidence of what?

MR. HOLLIDAY: Of damage to the marine environment in Alaska from drilling fluids, drilling operations? Just a yes or no will do fine.

CHAIRMAN WENNEKENS: I will say, at the present time, I will defer that answer until--

MR. HOLLIDAY: Yes is shorter than deferring.

CHAIRMAN WENNEKENS: Well, the problem is, what do we call damage and what do we call evidence?

MR. HOLLIDAY: I will be delighted to have you define it, sir.

CHAIRMAN WENNEKENS: Well, it takes more than just a yes or no answer on this.

MR. HOLLIDAY: Thank you.

MR. DENNIS G. WRIGHT (Environment Canada, Winnipeg, Manitoba, Canada): If solids removal equipment was 100 percent efficient, there would not be any need to use the vast quantities of drilling fluids that you do use in a hole; you could probably get by with that which is in the active mud system. Could you comment on this, please?

MR. ALLRED: Well, you are asking for something that is almost impossible. You have to remember that during the surface hole we are removing between 5 and 10 tons of materials per hour.

Yes, if the efficiency were 100 percent, I imagine you could. We try to make it as accurate as we can, but we do not have those types of machines.

It is a good point. I wish we had that type of equipment but, unfortunately, we do not.

HANDLING AND TREATMENT
OF OIL-BASE DRILLING MUDS

W. C. McMordie, Jr., Ph.D.*

Abstract

Oil-base drilling fluids are specialized muds which account for 5-10 percent of the total mud usage. They are used for productivity and in drilling operations in which water-base muds do not perform satisfactorily. Oil-based muds contain diesel oil, inorganic solids, surface active agents, asphalt, and water. Rig site handling is a two-part problem--treatment of mud and treatment of cuttings. Mud is contained in a closed system during drilling operations, then returned to the mud plant. Methods of handling and treatment of cuttings are: (1) containerize all cuttings and return to mud plant for authorized disposal, (2) wash cuttings, and (3) burn oil from cuttings. Descriptions of these methods are presented.

INTRODUCTION

Oil-base drilling fluids are specialized muds which have been in commercial use for 33 years. Originally, they were used as completion fluids to obtain greater recovery of petroleum from water-sensitive producing formations. The advantage of oil-base completion fluids for these productivity applications has been verified by the Bureau of Mines Oil-base drilling muds are stable at high temperatures and do not react with the formation. Because of these properties, oil-base muds have also been accepted as drilling fluids for high temperature wells, acid gas areas, water-sensitive shale, and salt drilling. Since oil-base fluids provide protection against corrosion, they are used as a protective pack for casing. Another major use of oil-base drilling muds is freeing drill pipe stuck in water-base drilling mud. Oil-base muds account for 5-10 percent of the total mud usage.

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COMPOSITION

Basically, oil-base drilling muds are a suspension of oleophilic colloids in a continuous diesel oil phase. Barite is used to adjust the mud density. Surface active agents are added to emulsify water and oil-wet the barite and drill cuttings. Each mud company has proprietary formulations for its oil-base drilling muds. Nevertheless, some generalizations concerning compositions are possible.

The oleophilic colloids function as viscosifiers, gelling agents, and filtration control additives. Examples of these colloids are air-blown asphalt, emulsifed water, and quaternary ammonium-substituted clays. The water-in-oil emulsifiers generally used are oil soluble calcium soaps of fatty acids, naphthenic acid, and/or tall oil acids. Modified fatty amines, polyethoxylated compounds, and sodium sulfonates are examples of the dispersing surfactants that oil-wet barite and drill solids. Many oil-base muds contain hydrated lime which is used for the in situ formation of the calcium soap and as an acid gas scavenger.

HANDLING AND TREATMENT

Modern drilling rigs are equipped to protect the environment and conserve mud. Catch pans are placed under the rig floor and the drill pipe rack. A valve is placed in the top of the drill string so that spillage will be minimized when additional lengths of pipe are added and when the drill string is pulled out of the hole. Oil-absorbant materials are used to clean up any minor spillage. Oil-resistant pipe wipers are used to clean the outside surface of the drill pipe. These precautions are taken so that the drilling fluid can be contained in a closed system.

Oil-base drilling mud is normally delivered as bulk liquid mud in tank trucks or boats. At the rig site, the liquid oil-base drilling mud is pumped through oil-resistant hoses into steel mud pits. Catch pans are used at connections. Usually, water-based drilling fluids are used to drill the upper part of the well. Therefore, the water-base mud in the hole must be displaced in order to drill with oil-base mud. During the displacement operation, a water-oil interface is obtained. The interface is pumped into a standby truck or boat and transported to the mud plant for authorized disposal.

As drilling begins, mud is circulated through the hole to bring the drill cuttings to the surface. The treatment of oil-base drilling muds now becomes a two-part operation--handling of the mud and handling of the drill cuttings. The mud and cuttings are allowed to flow over a shaker in order to obtain an efficient separation. It is imperative that a high-speed multiscreen shaker be used so that the maximum amount of mud can be removed from the surface of the cuttings. Unlike water muds, oil muds do not make mud from drill solids. Therefore, the volume of the oil-base mud does not increase during the drilling operation. In fact, as new hole is made, mud must be added to maintain the necessary volume. While circulating mud is in the pits, colloids, surfactants, and/or diesel oil are added, if required, to maintain the mud properties.

In addition to the antipollution regulations, there is a strong economic reason to keep oil mud contained. Economics have caused conservation of oil-base drilling mud long before the national concern over environmental protection. An oil-base mud system can cost over $100,000. However, after the well is completed, oil-base drilling muds are returned for credit. Thus the apparent high initial cost can be substantially reduced by careful handling practices.

Upon completion of the well, a portion of the oil-base mud is gelled and left in the hole as protection for the casing. The remaining mud is removed from the drill site and returned to the mud plant. The returned mud is treated, if necessary, and then reused.

The environmental problem with oil-base drilling muds arises from disposal of the cuttings, since an oil coating remains on the solids. In drilling 100 feet of 8-1/2 inch hole, 40 cubic feet of drill cuttings may be generated. As a rule of thumb, this volume of cuttings will be contaminated with 20 cubic feet of oil-base mud. Therefore, the handling problem with cuttings is the removal of oil from a nontoxic solid so that the environment remains free from contamination.

The handling and treatment of cuttings will be determined by the location of the well. On land locations, cuttings are collected in an area that is protected by an earthen dam. After the drilling is completed, cuttings are buried or burned in an approved area. For inland waters, cuttings are collected in a gondola barge. On completion of the well, the barge is towed to shore and the cuttings are disposed of in an approved area.

Three methods have been used to handle cuttings on offshore rigs--burning, cleaning, and collecting. Burning removes all hydrocarbons so that the cuttings can be dropped overboard. However, in most cases, supplementary fuel is required since the cuttings do not contain sufficient combustible materials. A sophisticated incinerator is required for safe operation and prevention of air pollution. This has been used in Europe for several years.

Cleaning cuttings consists of catching the cuttings as they come off the shaker and conveying them to the rig cleaning plant. Contaminated cuttings are washed in a diesel oil-surfactant solution and then mixed with water in a holding tank for separation. After oil, water, and solids separate, the oil is recirculated into the cleaning system, the water and cuttings pass over a shaker, the cuttings are dropped overboard, and the water is recirculated into the cleaning system. After the mud concentration in the diesel oil reaches a predetermined level, the diesel oil-mud solution is added to the oil-base drilling fluid, and fresh diesel oil-surfactant solution is added to the cleaning system. This method must be closely monitored to insure hydrocarbon-free cuttings.

In the collecting process, the cuttings are collected as they come over the shaker and are placed in containers. For ease of handling, the containers are 30-50 cubic feet in capacity. After the containers are filled, they are sealed and transported by boat to a land location, to an authorized disposal area. Of the three methods discussed, this method is the safest, both for environmental and personnel protection. However, transportation scheduling and limited rig storage may present a logistics problem with the cuttings collecting method.

There is a need for oil-base muds to prevent damage to the producing formation and when difficult problems are encountered. With proper care in treatment and handling of mud and cuttings, oil-base drilling mud can be used without endangering the environment.

DISCUSSION

MR. HARRY L. HARRISON: (A C Drilling Specialties, Odessa Texas): I would like for you to point out to the panel, if you would, the phase in which these oil-base muds come into the drilling operation. At what point in the drilling operation are they normally entered?

DR. McMORDIE: Oil muds are used deep down in the hole; normally, the surface hole is not drilled with oil muds. Probably the last 2,000 or 3,000 feet of drilling would be all that would be drilled with the oil muds.

MR. ROBERT B. ALLRED (Sun Oil Company, Richardson, Texas): Warren, let me help you a little bit. Many people have asked me to tell them what kind of drilling fluids we begin the hole with. Usually, the first thing we do when we get to a site is to drill a water well because we must have water when we start any hole, unless we air drill it or gas drill it. Then we usually just start with plain water, maybe with a little sodium or bentonite in there, sometimes for depths to 7,000 feet.

What I am trying to point out is in the areas where you have your runoff waters and where contamination might be taking place, the drilling fluid is usually only water; it does not contain any lignosulfonates, lignite, or any poisons. At best, it contains gel from the earth, and water from the earth.

Oil is used, as Warren pointed out, very deep, but we do not need an oil mud to start a well with. Oil muds are expensive.

If you use an oil mud on the well, you are usually talking about $100,000, sometimes as much as $500,000. So you only use it when you must because it is expensive.

DR. McMORDIE: Not only is it expensive, the crews do not like to use it either.

CHAIRMAN WENNEKENS: You mentioned that you take the residue to an approved disposal site. Can you give us a little detail on that?

DR. McMORDIE: I am afraid I am going to get into somebody else's talk if I do, but I can give you an example of what our company does in Louisiana.

We have burning sites that have been approved by both the parish and the State of Louisiana. The cuttings, or sludge, is taken there and burned.

MR. DENNIS G. WRIGHT (Environment Canada, Winnepeg, Manitoba, Canada):

When you spot diesel oil to free stuck pipe, I imagine the diesel gets very emulsified as it is coming to the surface. How do you separate that out from the system?

DR. McMORDIE: There are two ways you can handle stuck pipe applications. One of them is by complete displacement; that is, the entire mud in the system is displaced after the pipe is free, then the oil mud is removed from the hole and water mud is placed back in. Normally, spacers are used; that is, water between the oil mud and the water mud. The delivery vessels, either the boat or truck, carry all of this back to the mud plant where it is treated.

The second method is to spot, say, a hundred barrels of oil mud in the hole opposite the stuck pipe area. In this case, some mud is emulsified in the hole; however, when you get it free, the majority of the oil is removed and returned to the mud plant.

But, yes, you are correct; some oil mud is emulsified in the water mud.

MR. DONALD W. SOLANAS (U.S. Geological Survey, Metairie, Louisiana): I do not want to cut into Warren's business, but I feel that I must comment, again, that oil-base muds are not permitted to be used in the offshore operation on Federal areas. They can only be used under special problem instances. They can only be used by special permit approved by the U.S. Geological Survey.

Also, the generalization that in the bottom 2,000 or 3,000 feet of a hole is where oil-base muds are usually used does not mean that oil-base muds were used in the bottom 2,000 or 3,000 feet of every one of the 20,000 wells that have been drilled offshore. I would roughly estimate that 99-44/100 percent of wells drilled use water-base muds.

DR. McMORDIE: Yes. That is something I have written here, but I did not read it.

USGS regulations are that no oil muds will be used for drilling offshore unless a special application is there, and unless special permission is received.

In addition to that, no oil will be dropped in the water.

Oil muds are a specialized mud. They are used in 5 to 10 percent dollar volume of the mud industry, as best we know. As Bob said, they are extremely expensive, so that makes their physical use much less than that. They are used only when water muds do not perform satisfactorily. The application has to be an extremely specialized one.

MR. DALE P. VOYKIN (Pennsylvania Department of Environmental Resources, Williamsport, Pennsylvania): I heard one gentleman over here say that shallow aquifers are drilled through with water. You say that the oil-base muds are used at depth. What protection do we have for a shallow water table aquifer with the underlying impounding that you showed in your slides?

DR. McMORDIE: By the time the oil mud is in the hole, there are normally two strings of casing that have been set down and cemented across the shallow water aquifers.

MR. VOYKIN: In the pits, the reserve pit.

DR. McMORDIE: Yes.

MR. BRECK STRAUGHAN (A C Drilling Specialties, Odessa, Texas): We pretty well solved this in West Texas. We line our pits with polyethylene plastic to keep the contamination from going into the ground.

DR. McMORDIE: There have been some applications in which the cuttings, themselves, were caught in metal containers.

DR. RAYMOND W. MILLER (Utah State University, Logan, Utah): I do not know anything about muds; but I know if you are going to put in the bentonite solution, you are not going to get much water infiltrating to that pond bottem. By the time you get the oil mud in there, it is likely to be even worse. So I agree that there is not going to be any movement of water through the pond bottom.

MR. JAY P. SIMPSON (Baroid Division, N L Industries, Inc., Houston, Texas): Perhaps there is a misconception here, Warren. The oil and mud are not put into the reserve pit. You would have to handle just the cuttings. You do not put the oil mud out into an earthen pit; that is kept in steel tanks.

DR. McMORDIE: Right.

MR. JOHN R. JIMINEZ (EPA - New York): I have noticed (a little sarcasm here) that bird feathers have been used at times in drilling muds for special purposes.

Now, my question is, do these bird feathers get into the soil pits accidentally or are they put there for a special purpose? What I am really trying to ask is, what protection do you have for wildlife to prevent them from mistaking these pits for lakes?

MR. HARRY L. HARRISON: On a rig, these things run 24 hours a day, 7 days a week, holidays not excepted. Those big old motors up there make noise, and they pretty well keep all wildlife away in West Texas. Now, I don't know about your Louisiana swamps, but they will do it out in Texas.

MR. JIMINEZ: That may be true in Texas. I know the Audubon Society has been concerned that a lot of the migratory birds have mistaken oil pits for lakes, and have actually landed in them. Quite a lot of birds have been lost this way.

I know they are trying to use flares and guns for noise, but they are still having problems. And I want to know exactly what the industry proposes to do in some of these areas in the Central United States where, when you fly over one of these pits, you cannot tell if they contain oil or water.

Are you going to put scarecrows up there to keep away the birds?

DR. McMORDIE: These pits are water pits. I hope I did not leave a misconception that we have got oil out in an open earthen pit.

There are lights around these things, there is noise, there is human activity.

Personally, I think it is very unlikely that you will see any kind of animal or bird life around the pits.

I have been on a rig in Alaska up on the North Slope and the small amount of animal life I did see was extremely careful not to get around the activity, noise, humans, et cetera.

A PARTICIPANT: There are millions of birds here during the spring and winter. They are a nuisance. How do you get rid of them?

MR. JIMINEZ: Well, the proposal from the Corps of Engineers was to drop a solution on the birds and very nicely freeze them to death. If that is what you like, that is fine, but that is an opinion.

MR. GLEN W. ANDERSON (Standard Oil of California, Oildale, California): I think we have lost perspective on this drilling sump idea, in that this is a very temporary thing that is only used at the time that the well is being drilled. As soon as the rig equipment is moved out, the sump is disposed of and covered up, and the land is put back as was.

Further, in California we have a certain number of production sumps left that we are able to use to dispose of production water and things like this. However, we have, over the past 2 or 3 years, reduced these in number by at least three-fourths. The ones that we do have left are completely fenced with a very fine hog wire fence, and they are covered completely with a netting to prevent the birds from getting into them.

MR. SOLANAS: Just one comment on the question by the gentleman from EPA from New York on the feathers subject. The feathers that are used are for loss of circulation problems. They do not come from birds landing in the mud pits. They are probably chicken feathers from chicken-plucking operations.

WASTE WATER BASE DRILLING FLUID DISPOSAL

Dr. L. R. Louden and
R. E. McGlothlin*

Abstract

In 1970 a new patented process was developed for disposal of thick, watery fluids into a nontoxic and safe material that is environmentally attractive. This process is based on reactions between soluble silicates and silicate setting agents, which can be reacted at controlled rates to solidify mud and cuttings. This paper investigates drilling fluid disposal and its effects upon the environment. It reviews the nature of past and present drilling muds, discusses the contemporary disposal methods, and investigates the results of pollution tests conducted.

INTRODUCTION

Strong concern for our environmental quality has been growing in public importance the last several years. Preserving our environment presents industry a research and development challenge to create effective products and adequate disposal methods. This paper investigates drilling fluid disposal and its effects upon the environment. It reviews the nature of past and present drilling muds; it discusses the contemporary disposal methods; and it investigates the results of pollution tests conducted.

Traditionally, disposal of water-base muds was not a difficult process. Typical drilling fluid was composed of fresh or salty water, bentonite, barite, drill solids, and drilling chemicals, all basically inert. Thus, in many cases a mud pit, after drying over a period of

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time, was covered with overburden or spread onto surrounding land and disked into the soil. Offshore, drilling mud was sometimes pumped to the ocean bottom through a spreader pipe for disposal.

With the recent development of more stable mud systems that provided fluid stability under extreme pressures and temperatures, classical disposal systems were esthetically objectionable. Mud pits could be unsightly and persistent.

When drying, drilling mud forms a surface crust that retards evaporation. Additionally, the mud will not dry by subsoil leakage, and therefore a holding pit of mud may require several years to dry completely. Environmentally, the traditional method of pumping onto a field and plowing it under when dried is not compatible with present-day philosophy of proper disposal.

Four years ago a major engineering development project was initiated by Dresser's Swaco Operations to study effective mud and cuttings disposal. Several processes which included both mechanical and chemical disposal methods were investigated. Mechanically, a system was developed with four burners, each of one million Btu capacity, that would sinter drilling mud at a cost of $9-12 per barrel. Burning water-based drilling mud, however, was deemed uneconomical.

Chemically, a new technique was developed to solidify drilling mud and cuttings into a nontoxic and safe material that is environmentally attractive. This patented process is based on reactions between soluble silicates and silicate setting agents which can be reacted at controlled rates to solidify the mud and cuttings. After solidification and curing, the material can be mixed with native soil with no plant growth detriment.

During the curing period, crystalline growth builds a "pseudo clay" material containing the same moisture content as the underlying soil with a very-low-humus subsoil basic compositon. In the initial phase of this process, a rapid reaction between soluble silicates and polyvalent metal ions produces insoluble metal silicates. These insoluble compounds are nontoxic and almost impossible to resolubilize because of the crystalline "pseudo clay" structure.

The second phase of reactions occurs between soluble silicates and the reactive setting agent. The rate of the reaction is proportional to the concentration of setting agent. Under a controlled rate, the reaction forms a reticulated solid matrix which acts as a sponge, entrapping and immobilizing drilling mud components (for example diesel oil) in the structure. This mud solidification process was studied to develop data on resultant solids chemical characteristics. Of prime importance was a measure of the chemical composition of solidified mud constituents before and after rainfall or water percolation.

No standard procedure approved by regulatory agencies existed; therefore, a reproducible test was required. An industry-developed test method was selected (refs. 1,2). This test method has been thoroughly evaluated, and results can be duplicated in accredited laboratories and also correlated with field results.

STANDARD LEACHATE TEST

(1) One hundred grams of the material to be leached is placed in a 40- by 600-millimeter column containing 1 inch of cotton and/or glass wool at the bottom interface.

(2) The material to be leached is placed into the column.

(3) The column above the material is filled with distilled water (the diluent used for ease of reproducibility).

(4) Diluent water is seeped through the solidified material at a rate of approximately 1 cubic centimeter of water per minute. The diluent water seeping through the solid material, called the "leachate", is collected.

(5) Leachate normally is collected in 100-cubic-centimeter portions. Every eight portions simulate approximately 25 inches of ground water passing through the material in the field. Larger portions can be collected, if required.

(6) Leachate portions of various composites are analyzed by atomic absorption, spectrographic, colorimetric, or wet methods (as required) to determine the concentration of any constituents leached from the material under analysis. Results are reported in ppm.

Analytical data illustrate that higher initial concentrations drop to less than 1 ppm within 1-2 days as the crystalline growth (curing) is initiated. Once the crystal growth is completed, the constituents do not leach out of the solidified mud.

In the initial test to predict long-term characteristics of produced solids, a 12-pound-per-gallon water-based drilling mud was solidified and used as landfill in a central Illinois farm where the drilling location was slightly subgrade following well completion and well head installation. Rather than fill with hauled dirt, solidified mud was used to build location grade, and covered with top soil. During this process, local agriculture agencies conducted extensive analyses and testing, including controlled agronomy studies. Results of agency and collaborative studies indicated that additions of up to 30 percent of solidified waste drilling fluid mixed with the area's black soil caused no detrimental effects on plant development or crop life. Further, properties of this solidified mud tended to approach that of the host soil. There was no harmful effect to corn, soy bean, or other crops.

Another field test under different circumstances was conducted in Grand Isle, Louisiana. A southernmost extension of the State into the Gulf of Mexico, Grand Isle is essentially a sand bar at the mouth of a bayou facing the Gulf with approximately 30 miles of swamp behind it. As a major oil industry marine base, the island has a large mud disposal pit. Hurricane or other threats causing rising water which could displace mud made it imperative to develop alternative methods of mud disposal.

The holding pit contained mud from offshore marine rigs and large barge-mounted marsh rigs and had a 28 percent oil content.

The following is an analysis of the mud before solidification:

Mud wt.	11.8 lb/gal		
% Oil	28%	Cr^{+++}	1 ppm
% H_2O	41%	Ni^{++}	1 ppm
% Solids	31%	Mn^{++}	1 ppm
pH	10.1	Fe^{++}	1 ppm
Ca^{++}	2,720 ppm		
Mg^{++}	4 ppm		
Na^{+}	5,800 ppm		
Cl^{-}	13,100 ppm		
$SO_4^{=}$	870 ppm		
K^{+}	230 ppm		
Zn^{+}	2 ppm		

New disposal procedures used mud as area fill behind the bulkheads and at tank sites as dike material. Several alternate fill techniques were studied including using solidified material mixed with local fill; also, solidified mud was poured directly from the solidification unit into forms, much as a wall or dike might be poured from cement. Although the structural strength of solidified mud is not great, in poured and undisturbed states it demonstrates superior qualities over conventional earth tamping techniques. Solidified mud was also tested as a low permeability vertical wall because of its oil retentive claylike structure.

A long-term leaching analysis was run on the solidified Grand Isle mud with the following results:

LEACHATE ANALYSIS (Days)
Equivalent inches of rain
(Curing time 48 hours before leaching began)

Constituent	1 Day	2 Days	8 Days	15 Days	28 Days
pH	12.1	12.3	12.0	11.8	10.6
Oil	<1.0	<1.0	<1.0	<1.0	<1.0
Ca++	420	400	260	220	120
Mg++	<.1	<.1	<.1	<.1	<.1
Na+	2,100	2,000	20	10	10
Cl^-	2,750	2,600	10	10	8
$SO_4^=$	50	40	9	3	2
K+	90	40	5	3	2
Zn++	<.1	<.1	<.1	<.1	<.1
Cr+++	<.1	<.1	<.1	<.1	<.1
Ni++	0	0	0	0	0
Mn++	0	0	0	0	0
Fe++	0	0	0	0	0

The required concentrations of silicate reactants and setting agents vary considerably depending on (1) the composition of the slurry to be solidified, (2) the physical characteristics required for the final solidified materials, (3) the time allowed for setting to occur, and (4) the conditions present during the setting period. Required quantities are determined by pilot testing the mud to be solidified. Since the slurry and reactants mixture frequently has a high gel strength, it is imperative to add the activator after the setting agent has been mixed into the slurry.

Systems containing high concentrations of heavy metal ions require additional activators to complete the chemical reaction. Initially, the heavy metal ions are precipitated as a metal salt. This salt is then bound within the solid matrix of the solidified material and is not leached out by excessive rainfall.

To demonstrate this process, a 11.6 lb/gal laboratory mud was prepared with metallic ions commonly found in drilling muds. An excess concentration of these ions was added for this test.

The composition of this mud was:

Mud wt.	11.6 lb/gal
pH	10.0
Cr+++	1,388 ppm
Zn++	2,800 ppm
Mn++++	2,522 ppm
Co++	285 ppm
Fe++	13,300 ppm

An analysis of the filtrate showed:

pH	8.3
Cr+++	550 ppm
Zn++	60 ppm
Mn++++	210 ppm
Co++	3 ppm
Fe++	100 ppm

This system was then solidified and leachate analysis taken after each established curing time: (1) 24 hours, (2) 48 hours, (2) 96 hours, (4) 168 hours (7 days), (5) 336 hours (14 days), (6) 672 hours (28 days).

After each sample had cured the predetermined time, 100 ml of leachate were taken each day for 28 days. The data illustrates that following only 1 day of curing, less than 0.1 ppm of the metals leached out.

LEACHATE ANALYSIS

Equivalent inches of rain

	Cured 1 day			Cured 7 days			Cured 28 days		
Constituent	1	7	28	1	7	28	1	7	28
Cr+++	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Zn++	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Mn++++	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
CO++	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Fe++	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1

CONCLUSIONS

Mud solidification is an excellent disposal solution for most drilling operation byproducts. The attractive advantage is that this disposal system of chemically reacted and solidified materials is nonpolluting and environmentally safe.

The pseudo-clay material resulting from the crystalline growth, encapsulation, and dehydration, can be employed for numerous applications, including for reclamation landfill and for treating a large variety of industrial wastes. When used in agricultural fill restoration, seed germination studies conducted by an independent agronomist indicated that germination was not affected in garden soil which included up to 40 percent of solidified mud, and germination was retarded only a few days in soils containing up to 80 percent.

Cost factors determine the necessity for adequate solids control equipment and processes. This mud solidification process costs about $3 per barrel, and portable systems capable of processing 1,000 barrels a day are available. Correct solids handling equipment and proper drill site drainage can reduce mud volumes to be solidified as much as 75 percent, significantly reducing drilling fluid disposal costs.

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DISPOSAL OF DRILLING FLUIDS
AND DRILLED-UP SOLIDS
IN OFFSHORE DRILLING OPERATIONS

W.J. McGuire, Ph.D.*

Abstract

Water-base drilling fluids are used predominantly in offshore drilling operations. Fluids containing oil are resorted to only where special problems necessitate their use.

Since OCS Order No. 7 was issued August 28, 1969, drilling fluids containing oil have been transported to shore and have either been stored for future use or disposed of in landfills. Most oil-coated solids were also disposed of on shore. Some recent attempts to clean the cuttings for offshore disposal have succeeded.

Many offshore lease agreements stipulate that drilled solids must be discharged at a distance no greater than a designated distance from bottom (usually 20 feet). These stipulations are imposed in estuaries and near reefs.

All rotary drilling operations require that a fluid be circulated while the bit penetrates the encountered formations. In almost all cases, this circulation is down the drill pipe, out through ports in the drill bit, across the bottom of the hole where it sweeps up the cuttings generated by the bit, then up the annulus between the drill string and the hole.

In the basic drilling operation, the returned drilling fluid is first passed through a vibrating screen called a shale shaker, where most of the drilled solids are removed from the system. Then the fluid passes through a setting tank, where the small particles of rock which passed through the shale shaker screen settle to the bottom. Ultimately, the fluid is picked up from a suction pit by the slush pump and then put back down the drill pipe.

Besides removing the cuttings from the hole, the drilling fluid must maintain sufficient hydrostatic head to prevent the intrusion of formation fluids into the hole. If such intrusion is not prevented, the drilling operation quickly degenerates into a disaster called a blowout.

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Many deep formations contain fluids under a pressure that greatly exceeds the hydrostatic pressure gradient of water, 0.43 pounds per square inch per foot of depth. In some areas formation pressures have been observed to be as high as 0.9 pounds per square inch per foot.

As a result, drilling fluids must frequently have densities over twice as great as that of water. This is usually accomplished by adding a particulate weighting material to the system, most commonly barites ($BaSO_4$).

The addition of weighting materials to the system places another requirement on the drilling fluid--it must possess a gel strength. That is, the resistance to shear at zero rates of shear must be finite so that the barites will not settle when circulation is suspended. Hence, a colloidal system having a gel strength is required.

Colloidal suspensions are notoriously delicate. The array of over 200 proprietary chemicals is comprised mainly of colloid stabilizers. Most of these are tannins, lignite, and lignosulfonates.

Since the present price of barites offshore is about $94 per ton, very little drilling fluid is discarded. Most drilling fluids are stored for future use. However, when a water-base drilling fluid is discarded, it is usually disposed into the ocean with no attempt to salvage any of its components, despite the fact that the recovery of barite by centrifugal methods is a common practice on land.

Many lease agreements state that leases issued as a result of the lease sale will contain the following stipulation for the protection of high-relief offshore banks: no structures, drilling rigs, or pipelines will be allowed within the aliquot parts established for the offshore banks. In addition, operations on leases issued covering the tracts described as well as operations within the aliquot parts of the tracts will be restricted as follows: drill cuttings and drilling muds must be disposed of by shunting the materials to the bottom through a downpipe that terminates 20 feet or closer to the sea bottom. However, if the Supervisor, after consultation with the Manager, Gulf of Mexico Outer Continental Shelf Office and the Regional Director, U.S. Fish and Wildlife Service, Albuquerque, New Mexico, determines that the shunting method is not adequate to protect the unique character of the subject areas, then the Supervisor will require the barging and dumping of these materials a minimum of 10 miles from any of the above described aliquot parts of the seven banks. Should the barging method be required, disposal sites must be approved by the Supervisor, and any other agency or agencies having jurisdiction at the time.

The disposal of cutting through a downpipe poses some difficulties. Drilled-up sands and cuttings from many shales present no problem. But some drilled-up shales, marls, and clay are difficult to handle. These intractable materials react with water. The cuttings absorb large volumes of water, swelling to many times their original volumes. In doing so their density approaches that of seawater so they do not sink nearly so rapidly as a comparable piece of rock would. They also develop a sticky surface. The particles agglutinate and form an unmanageable sticky mass that will not move down the pipe spontaneously. Therefore, the downpipe must be equipped with high-velocity water jets which force the sodden mass to the bottom.

Because all drilling fluids must exert a hydrostatic head that exceeds the pressure in all of the fluids penetrated, there is a persistent flow of the liquid phase--or more generally, the continuous phase--into all of the permeable formations expossed by drilling.

This invasion of permeable formations deposits the solid fraction of the drilling fluid at the interface, where it forms a filter cake. Filter cakes are useful insofar as they help stabilize sand formations, which are not highly consolidated. But they create an ever present hazard, the possibility that drill pipe or drill collars will become embedded in the filter cake and become stuck. This so-called wall sticking is more complicated than its simple name implies. Figure 1 is a diagram of an open hole in a permeable formation. The filter cake has a thickness (t). The pressure in the formation is designated P_f, and the hydrostatic head of the drilling fluid, P_i, exceeds P_f by as much as 500 pounds per square inch. The filter cake is orders of magnitude less permeable than the formation. Therefore, it is the controlling restriction to flow. The entire pressure difference is exerted across the filter cake. For simplicity, it is assumed that the entire 500 psi in the example is exerted on the inside surface of the cake.

When a drill collar becomes embedded in the cake as shown, this pressure difference is exerted against the chord $\overline{AB}$. Considering moderately thick filter cakes in ordinary deep drilling situations, this chord length may be as long as 5 inches. Then each foot of embedded drill collar is pushed against the wall

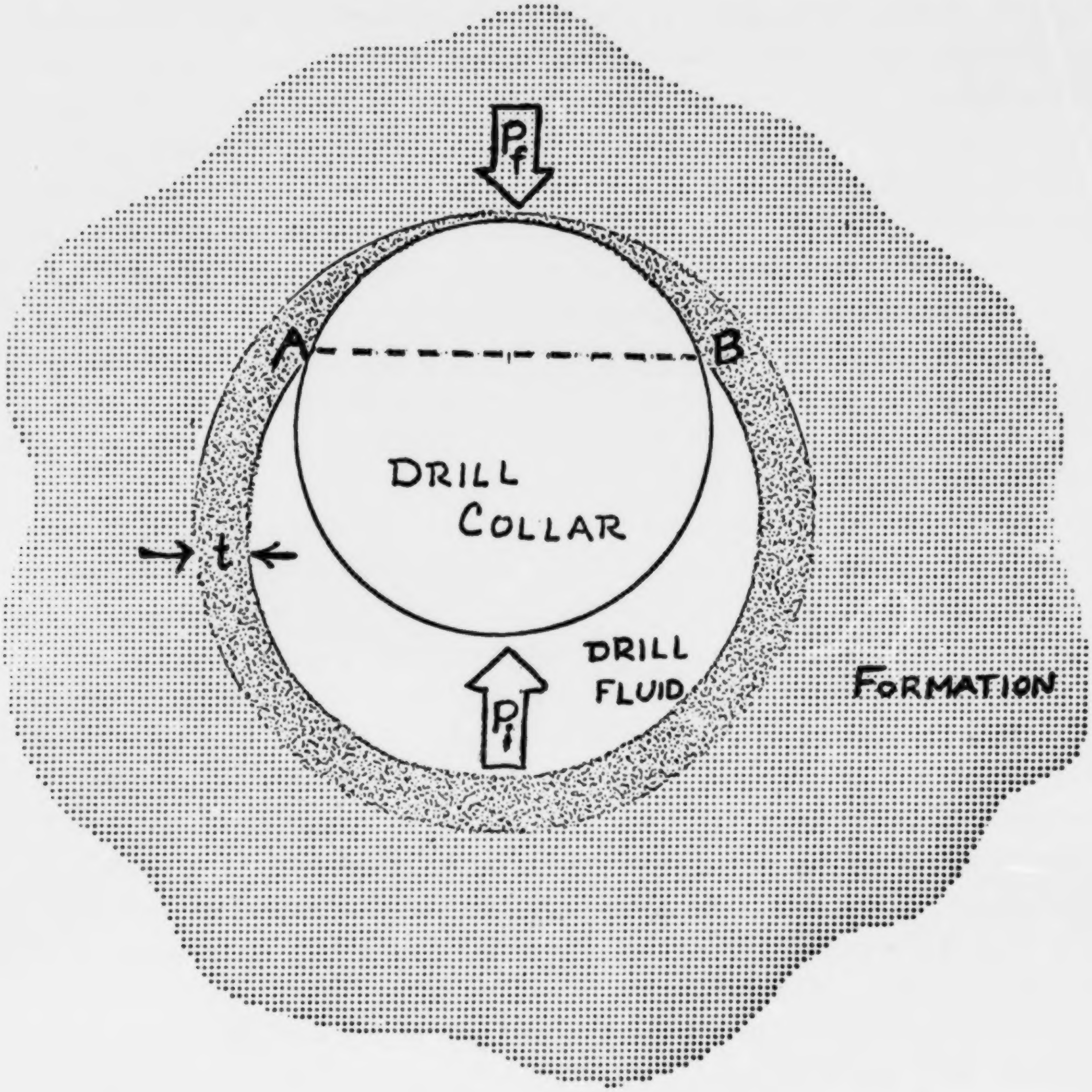
P_f
A
B
DRILL COLLAR
t
DRILL FLUID
P_i
FORMATION

Figure 1. Illustrating the mechanism of wall sticking.

of the hole by a force of 30,000 pounds. The coefficient of friction between steel and filter cakes has been determined to be in the vicinity of 0.5. Then a force of 15,000 pounds would be required to slide the 1-foot length of drill collar out of the cake.

When many wells are drilled from offshore platforms, one only is vertical. All the rest must be deviated from vertical. Many achieve angles as high as 70° from vertical. In such situations wall sticking is a virtual certainty.

When this occurs it is not uncommon to attempt to free the drill stem by spotting small quantities of special fluids over the stuck portion. These fluids are oils containing large quantities of chemicals that enhance their capability of wetting steel preferentially. Such materials invariably become dispersed throughout the drilling fluid system. OCS order No. 7 of August 28, 1969,* specifically prohibits the disposal of such material offshore. As a result, these materials were barged ashore and trucked to land fill disposal sites.

When wall sticking interferes too frequently with drilling operations, oil-base systems or inverted oil emulsions are employed. These systems deposit extremely thin filter cakes so that the chord of penetration is negligibly small thus subverting the sticking mechanism. Oil Base, Inc. "Black Magic" is a total oil system using diesel oil and asphalt. This mud system requires drill cuttings to be contained and transported to a disposal site onshore. The mud company is working to develop a drill cutting cleaning system. The present system requires a number of tanks and their size imposes a space requirement on offshore platforms, which restrict or prohibit its use during drilling operations.

Inverted oil emulsion mud contains from 60 to 80 percent diesel oil. It derives its name from the fact that oil is the external or wetting phase. The cuttings generated when either system is used are completely wet with oil.

If the expense of transporting the cuttings ashore (estimated to be $15,000 for a 20,000 foot well) is to be avoided, the cuttings must be cleaned.

Two approaches to this problem have been considered. The first was to burn the oil off by submitting the cuttings to a 4,000°F temperature generated by high-intensity lamps. In the pilot operation of this process, the cuttings were transported under the lamps by a stainless steel conveyor. The process was abandoned because of unequal exposure to the heat. Also it was feared that the high temperatures involved would be considered to be an unacceptably high risk by the insurers.

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*Drilling mud containing oil shall not be disposed of into the Gulf. Drilling mud containing toxic substances shall be neutralized prior to disposal. Drill cuttings, sand, and other solids containing oil shall not be disposed of into the Gulf unless the oil has been removed.

The second approach, washing the cuttings with a special detergent, appears to be a practical solution. Most washing systems are similar, but there are variations in equipment and techniques. Baroid Division of National Lead Industries has used three different schemes. One consists of a Medaris cuttings washer installed at the discharge of the shale shaker. Cuttings are directed into the washer through a funnel-shaped intake. As the cuttings pass through the washer they are tumbled in a revolving screen within the washing drum and are sprayed with the wash solution. When rig layout does not allow this arrangement, the cuttings are brought to the washer by an Archimedes screw. Clean cuttings are then discharged through the downpipe.

This system requires two 5-horsepower moyno pumps and a retention tank for the wash solution.

One Medaris washer can handle cuttings from a 9-7/8" diameter hole being drilled at 50 feet per hour. Larger holes and faster drilling rates require two washers.

Another system Baroid has used is built around a 50-barrel tank partially filled with a wash solution. Cuttings fall into the tank as they fall from a double-deck shale shaker.

The wash tank is equipped with a conventional mud-tank mixer that agitates the wash solution. A centrifugal pump circulates the wash solution and cuttings over a second double-deck shaker on top of one end of the wash tank.

As the wash solution is circulated over the second double-deck shale shaker, clean cuttings are discharged for disposal and the wash solution is completely shut down for a few minutes to allow the oily particles to settle.

In order to overcome an extremely difficult drilling and casing situation in the North Sea, Placid Oil Company required an oil mud. In order to satisfy the Netherlands restrictions on pollution, Placid installed a third Baroid cuttings cleaning system.

This system is a somewhat more complex cuttings washing system, and has been installed on a rig drilling for Placid Oil Company in the Dutch sector of the North Sea under the approval of Dutch authorities. The cleaning system is built around two double-deck shakers and a smaller shaker with the same vibrating motion as the rig units.

The two rig shakers accommodate full mud flow from the well. Drilled cuttings pass from these onto the smaller shaker, where they are thoroughly washed with a unique nonaqueous washing solution cirulated by a small centrifugal pump.

The washing solution is miscible with the oil mud being used, and after it becomes contaminated it is returned to the mud system.

One key to the effectiveness of this system is a sump arrangement through which cuttings are discharged to the ocean floor. The sump consists of a 20-inch casing, installed in one of the jack-up rig's legs, and extending almost to the ocean floor. Within this 20-inch casing is a 10-inch pipe that extends to about 30 feet above the bottom of the 20-inch casing. Cuttings enter the 10-inch pipe from the small shaker and fall through it into the 20-inch sump and onto the ocean floor.

Removal of any contaminants in wash solution remaining on the surface of the cuttings takes place during the fall through the 20-inch pipe, and any such contaminated wash solution is contained within the 20-inch pipe.

To remove accumulated contaminants from the 20-inch sump, a submergible pump is also run into the 20-inch pipe and placed near the water surface to pump oil contamination from the sump.

Oil contaminants from both the submerged pump and from the cuttings washer are routed to an oil/water separator. Oil from the separator is returned to the mud system; the water is discharged back into the sump. This "loop" provides a completely closed system.

The system can also accommodate any displaced mud that might pose a contamination problem. It is designed to handle almost anything that might release hydrocarbons.

In this particular installation, mud from the rig shakers goes directly through the main deck to the return mud system.

Conclusions

1. Water-base drilling fluids are preferred in offshore drilling situations to avoid oil contamination.
2. Oil-base drilling fluids are a frequent necessity to overcome extreme difficulties.
3. There are devices that clean cuttings generated in invert oil emulsion drilling fluids to government specifications.
4. All oil-base drilling fluids are disposed of by barging to shore.

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DISCUSSION

MR. JAMES B. JOHNSTON (Bureau of Land Management, New Orleans): I would like to say that concerning the margin of cuttings from drilling operations, that is one method. The other method you mentioned concerned the shunting of the materials to the bottom. On the Gulf of Mexico we have had two wells drilled, one in an area around the Florida middle ground, and one near the east flower gardens in Texas. In both of these operations there was shunting to the bottom. In the Florida area it was 50 to 60 feet from the bottom, and in Texas I think it was 20 to 30 feet from the bottom.

Also, let my say that shunting is not necessarily confined to fish banks. We are also concerned with coral areas, like the middle ground and the flower gardens.

The one case I would like to mention is in the Florida middle ground area, in which myself and three divers from the State of Florida (marine biologists) dove on the drilling location after the well had been drilled. We were unable to detect any of the cuttings in the immediate area, which I would say is 200-300 feet from the actual drilling spot. I later found out from the USGS people that they had talked to some divers from Texaco, who said that the cuttings had been confined to an area with a diameter of about 50 feet and 6 feet in height. As I said, we were unable to find any detected cuttings. We did find an empty drill cutting bag on the bottom so we knew we were in the area, based on our readings.

I think it was Mr. Scalan from the University of Texas who pointed out that we at the Bureau of Land Management are investigating this. Hopefully, we will be able to monitor some of these drilling operations (that is one reason Dr. Monastero is not here today) and solve some of the problems that have been raised at this meeting.

ENVIRONMENTAL EFFECTS OF DRILLING MUDS AND CUTTINGS

James P. Ray, Ph.D.,
and E. A. Shinn*

Abstract

In 1973, a Shell research group studied some of the environmental parameters concerning offshore drilling discharges. During a 2-day period in 1973, they collected 34 water samples around a Shell platform off the coast of Louisiana. Samples were taken at the surface (1 ft), midwater (120 ft), and at the bottom (245 ft). The platform was actively drilling at the 9,000 ft level with lime base mud at the time. Analyses were made for alkalinity, total dissolved solids, total suspended solids, total organic carbon, and total dissolved chromium. Results indicate that all parameters approached normal background levels as close as 60 yards to the platform. Mid- and bottom-water samples beneath the platform showed some detectable chromium, but hexavalent chromium was not detected in any samples.

Theoretical dilution curves were estimated for a current of 0.5 feet per second and dishcarge rates of 40 and 250 barrels per hour. Dilutions of 1,000:1 were estimated at approximately 1,000 and 10,000 feet, respectively.

The importance of environmental observations is stressed. Mr. E. A. Shinn, an experienced diver and underwater photographer, has observed marine life under Gulf of Mexico platforms for many years. He has observed that the light mud fractions appear to drift upward and laterally, while the cutting chips and filter cake fall straight to the bottom. Encrusting organisms are observed prolifically covering platform structures. Barnacles are seen living on and inside discharge downpipes. Fish swim through discharge material with no observable ill effects.

There appear to be no visual detrimental effects of drilling discharges to organisms that are living above the bottom. Cutting piles beneath production platforms have been observed to be repopulated with marine communities.

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Introduction

This paper is directed at two topics. First is the presentation of some preliminary work by Shell which indicates that discharge concentrations in the marine environment are very low. This research conducted in 1973 compares favorably with that of Zingula (ref. 1) in late 1974 at a different location.

Second is the importance of good environmental observations by qualified people. Mr. Gene Shinn of the U.S. Geological Survey has spent much of his career underwater, observing and photographing the marine environment. Some of his comments are presented here.

Preliminary Field Study

In 1973, a Shell team engaged in a study to answer some of the questions concerning platform discharges. An offshore Louisiana platform situated in 245 feet of water was chosen. A 2-day water sampling program was conducted during the lime-base mud phase of drilling at the 9,000-foot interval. Sampling stations were selected on all sides of the platform (figure 1). The discharge pipe was located 35 feet below the surface.

Water samples were taken at the surface (1 ft), midwater (120 ft), and the bottom (245 ft) using an underwater air displacement type sampler. Water samples were analyzed for alkalinity, total dissolved solids, total suspended solids, total organic carbon, and total chromium.

The results of these analyses can be seen in tables 1 and 2. The most important conclusion that can be drawn from these data is that the concentrations found around the platform are comparable to normal background levels as reported by Zobell (ref. 2) and Dryssen et al. (ref. 3). Data presented by Zingula (ref. 1) at the Environmental Impact Hearing in Trenton, New Jersey, and at the Conference on Environmental Aspects of Chemical Use in Well Drilling Operations (1975) in Houston, Texas, confirm this observation.

Alkalinity, expressed as part per million calcium carbonate, ranged from 123 to 130 ppm. This lies within the background levels given by Dryssen et al. (ref. 3) of 120 ppm and Zobell (ref. 2) of 200 ppm.

Due to a difference in analytical techniques, values in tables 1 and 2 for total dissolved solids appear high when compared to literature

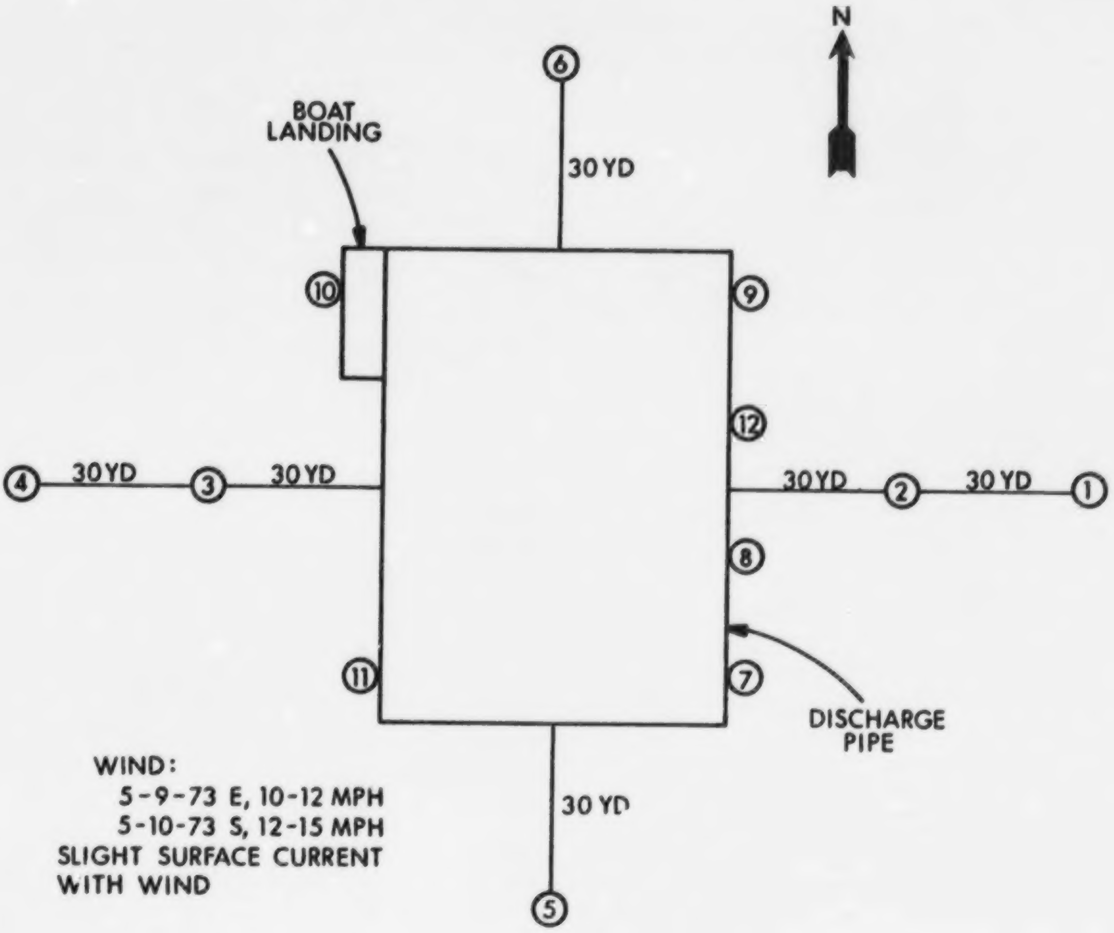
N
BOAT LANDING
30 YD
⑥
⑩
⑨
⑫
④
30 YD
③
30 YD
30 YD
②
30 YD
①
⑧
⑪
⑦
DISCHARGE PIPE
WIND:
5-9-73 E, 10-12 MPH
5-10-73 S, 12-15 MPH
SLIGHT SURFACE CURRENT WITH WIND
30 YD
⑤

Figure 1. Seawater sampling points.

values of 34,325-35,100 ppm. Filtered samples were evaporated to dryness at 60°C instead of 180°C as recommended in the standard methods. This was done for laboratory convenience, since a 180°C oven was not available. As a result, the dissolved solids numbers are consistently high, probably due to a fair amount of water of hydration bound to the salt crystals. A sample was dried at both temperatures: 60°C which yielded 41,500 ppm, and 180°C which yielded 36,200 ppm. It was determined that 60°C results could be corrected by multiplying by the constant 0.872.

The values for total suspended solids are very low as would be expected for offshore waters (> 100 miles). Zingula's data (ref. 1) showed

Table 1. Analysis of seawater around platform

May 9 Wind E 10-12 mph location	Depth	Alkalinity (ppm as $CaCO_3$)	Total* dissolved solids (ppm)	Total suspended solids (ppm)	Total organic carbon (ppm)	Total chromium (ppm)
1	1	125	43500	8	5	ND (0.01)
	120	123	42600	20	9	"
	245	125	44100	16	5	"
2	1	123	41700	8	5	"
	120	123	41200	80	6	"
	245	125	41800	0	7	"
3	1	123	42600	20	5	"
	120	125	47900	40	10	"
	245	125	45300	0	6	0.04
4	1	123	42200	0	5	ND
	120	125	42200	0	5	"
	245	123	42300	0	7	"
5	1	123	41800	4	4	"
	120	123	44700	0	7	"
	245	125	43100	28	6	"
6	1	123	42300	8	5	"
	120	125	42200	0	7	"
	245	123	42700	0	16	0.01
9	1	125	42400	0	6	ND
	120	125	41800	0	8	0.038
	245	125	42100	0	6	0.01
10	1	125	42300	0	7	ND
	120	130	40400	0	7	0.052
	245	123	40900	12	5	ND
12	50	125	41500	8	6	ND
	120	125	41300	0	8	ND
	245	125	41600	0	7	ND

*Determined by evaporation at 60°C. See text for explanation.

a surface value of 5.2 ppm for clear waters upstream from the drilling platform.

Many people have voiced concern as to turbidity effects on the marine organisms. It appears from the data gathered that suspended sediment loads are rapidly diluted and reach background levels close to the platform (see total suspended solids, tables 1 and 2). It is interesting to note that

Table 2. Analysis of seawater around platform

May 10 Wind S 12-15 mph location	Depth	Alkalinity (ppm as $CaCO_3$)	Total* dissolved solids (ppm)	Total suspended solids (ppm)	Total organic carbon (ppm)	Total chromium (ppm)
7	1	123	41300	0	9	ND
	120	128	44000	0	7	0.038
	245	125	42500	0	7	0.01
8	35	128	41400	0	10	0.037
11	1	125	41500	44	4	ND
	120	130	40100	0	8	0.045
	245	123	44300	0	11	ND

*Determined by evaporation at 60°C. See text for explanation.

even though the sampling stations were close to the platform (i.e., 60 yards maximum), many of the samples have zero values for total suspended solids. Griffin and Ripy (ref. 4) concluded their studies on turbidity and suspended sediment concentrations as related to environmental impact of offshore platforms, with the following statement: "There was no detectable effect on turbidity, suspended sediment composition, or concentration produced by any of the offshore production platforms examined in this study (Gulf Universities Research Consortium). Therefore, although we may find them visually offensive, at least they do not muddy the water."

Considering the high chromium levels (trivalent) in ferrochrome lignosulfonate (30,000-40,000 ppm), it is significant that no hexavalent chromium was detected in any solid or aqueous sample. The analysis figures present in tables 1 and 2 are for total chromium. Despite the relatively high levels of chromium in ferrochrome lignosulfonate, it is significant to note that chromium was undetectable in most samples. Those samples with detectable chromium were taken from mid- and bottom-waters near the platform.

Discharges and Dilution

It is very important to understand what does happen to our marine discharges. If we know what happens to discharges, then we can correlate toxicant levels determined from laboratory bioassays with real levels actually existing in the marine environment.

It has been estimated that the average Gulf of Mexico 10,000-foot well produced 2 million pounds of solids. Contrary to the opinions of many nondivers, the solids (cuttings) do not form large, desert-like mounds on the sea floor. As has been shown by Zingula (ref. 1), the drill cutting piles are in reality, of low relief, and repopulated with marine organisms following drilling cessation. Zingula reported that no set rules exist to determine what the shape, thickness, and extent of cuttings accumulations will be. Side-scan records of wellsites in the Gulf of Mexico and Santa Barbara Channel show no definite shadows several months after drilling has ceased, indicating that the heights of cuttings piles are 6 inches or less. Shinn (ref. 5) stated that although a cuttings pile may be several feet thick and cover a half acre at the time of well completion, each major storm will disperse some of the material. Mr. Shinn found no cuttings beneath production platforms in 60 feet of water at the Buccaneer field 25 miles off Galveston, Texas, where drilling ceased approximately 10 years ago. Oetking et al. (ref. 6) observed the same thing in 66 feet of water beneath an offshore Louisiana platform that had ceased drilling 15 years previously.

It is of interest to compare man's contribution of sediments and solids to the Gulf of Mexico via drilling versus nature's contribution via the Mississippi River. Boykin (ref. 7) reported an estimated daily outflow of 2 million tons of sediment from the Mississippi River. In comparison, the average Gulf of Mexico well produced 2 million pounds of material during the approximately 2-week drilling period. This is 0.05 percent of the Mississippi's daily outflow, or in less than 2 days, the Mississippi deposits more sediments than the 15,200 wells drilled in the Gulf of Mexico.

Ocean currents are a major factor in diluting and dispersing offshore discharges. Shell has calculated a theoretical dilution ratio, R_D, which is the volume fraction of seawater divided by the volume fraction of discharged fluid at a particular location and time. Calculations were made for two discharge rates of drilling mud, 40 barrels per hour and 250 barrels per hour. The mixing depth was 245 feet and the current assumed to be 0.5 feet per second (0.29 knots). As can be seen in figure 2, a dilution ratio R_D of 1,000 to 1 would be expected at 1,000 feet downstream from the discharge. Figure 3 shows similar information for a 250 bbl/hr discharge rate, i.e., R_D 1000:1 - 10,000 feet downstream.

Dilution curves such as generated in figures 2 and 3 can assist us in putting TL_m data from laboratory research in proper perspective. Assume that the concentration of one of our discharge materials was 10,000 ppm with a 96-hour TL_m value of 1,500 ppm. The theoretical dilution curve in figure 2 indicates that approximately 40 feet downstream we would already have reduced our toxic material to about 100 ppm, which is far below toxic levels.

Environmental Observation

Environmental observations are an important ingredient in establishing an overall picture. Mr. Shinn of the U.S. Geological Survey, Miami, Florida, has spent many years diving in the Gulf of Mexico. His knowledge of the marine environment and underwater photographic abilities are well known. Through his pictures, the nondiver can begin to understand what is happening beneath the surface.

As the discharge leaves the downpipe, two components are obvious. The lighter sediments and clays rise vertically and horizontally to be dispersed by the current (figure 4). Heavier cuttings (fingernail size rock chips) fall straight to the bottom to add to the cutting pile (figure 5). Does the discharge have a detrimental effect on marine life? Yes and maybe! There is no doubt that sessile benthic organisms which cannot move about would be buried by the cutting pile of a drilling well.

It is important to note that the average Gulf of Mexico well takes 10 to 14 days to drill. Upon completion of drilling activities on a platform, the cutting piles are repopulated by many species of organisms as observed by Shinn (ref. 5), Zingula (ref. 1), and others (personal communications).

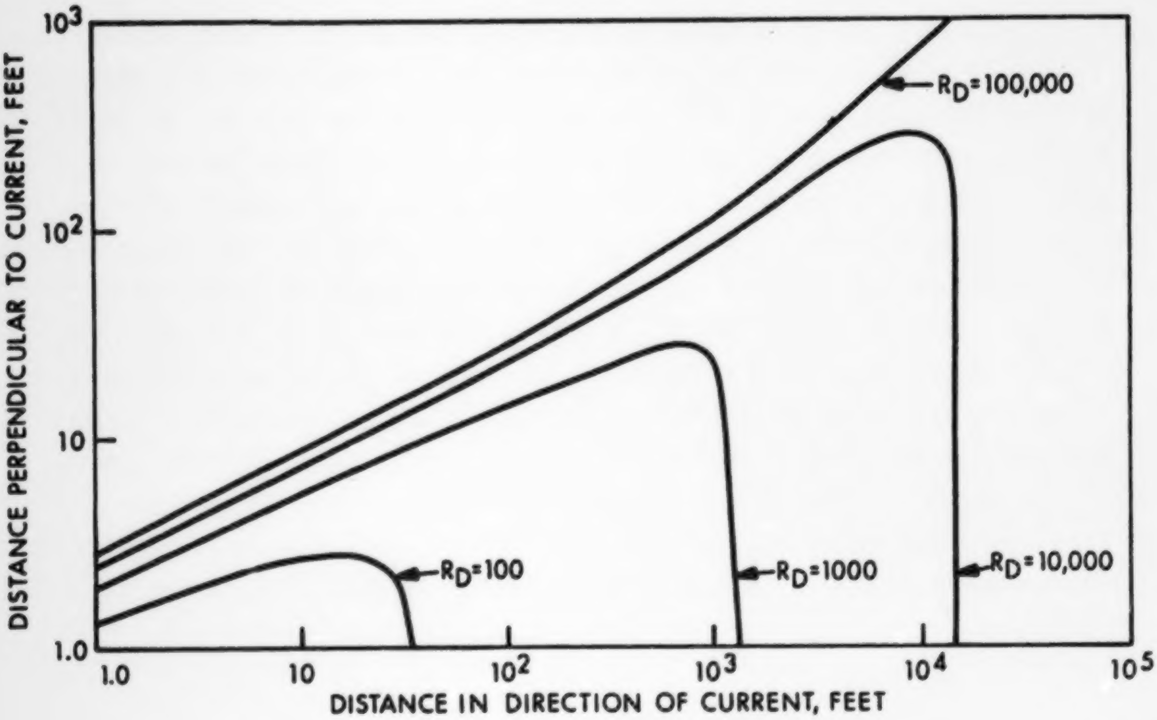

Figure 2. Dilution ratios at 40 bbl/hr.

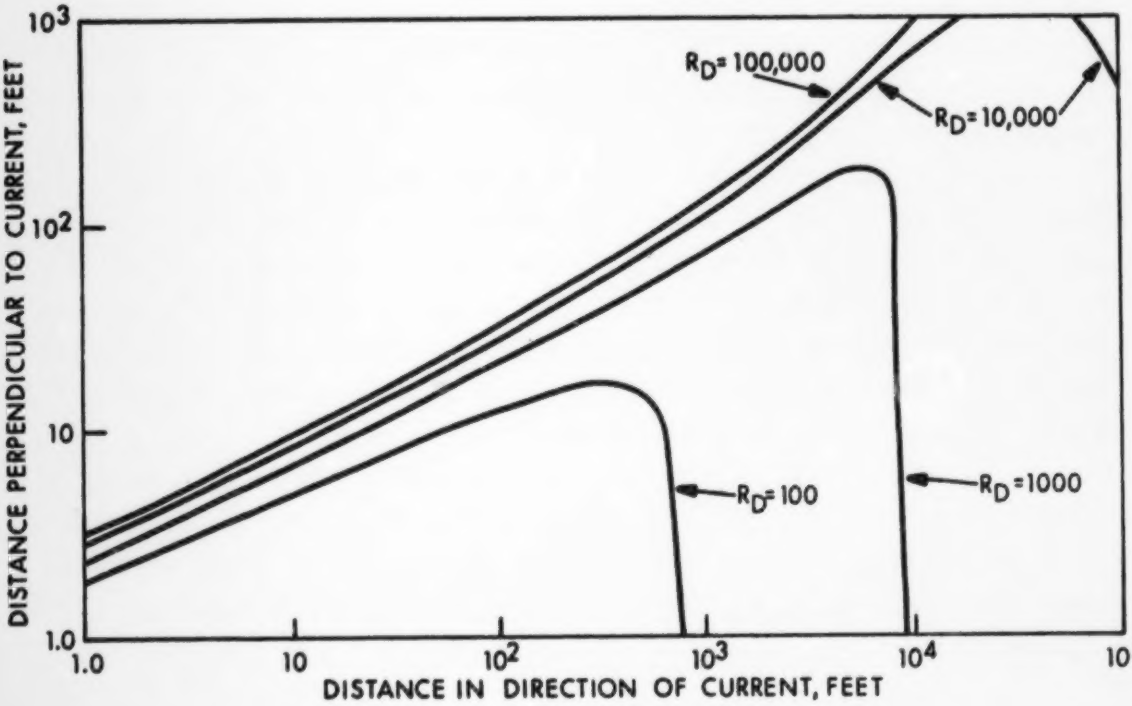

Figure 3. Dilution ratios at 250 bbl/hr.

Figure 4. Downpipe discharging at 20 feet. Light components of mud characteristically well upward and spread laterally. Barnacles can be seen growing on the outside and inside of the discharge pipe. A school of spadefish (Chaetodipterus faber) are seen swimming in the background.

Figure 5. This discharge is similar to that of the preceding photograph except that some of the heavier solids can be seen settling to the bottom.

Figure 6. This downpipe is discharging directly onto a cross member of the platform. Note the heavy encrustation of barnacles on all structures.

Figure 7. The flange around this conductor pipe shows no buildup of discharge material. Wave and current action disperses most material over a wide area.

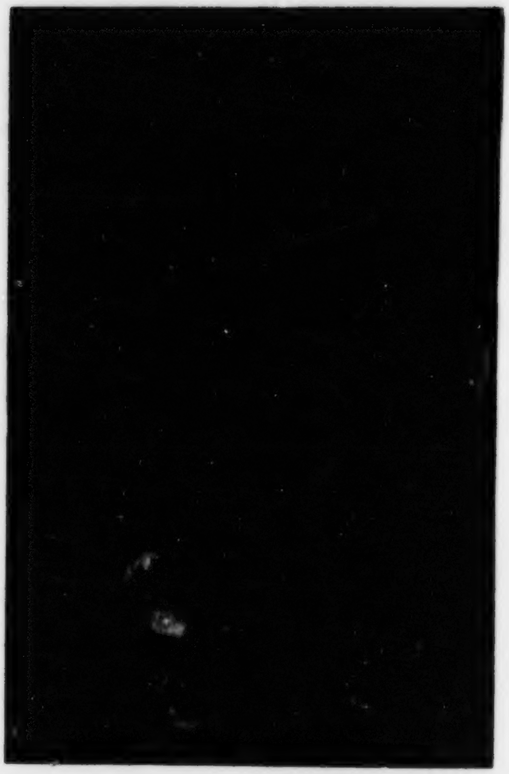

Figure 8. Looking upward toward the discharge pipe, a school of spadefish (Chaetodipterus faber) can be seen swimming through the falling cutting chips.

Figure 9. As noted previously, cutting chips and aggregated muds drop to the bottom while the light, turbid components disperse laterally. A barracuda (Sphyraena barracuda) cruises in the background.

In depths below the effects of wave action, the cutting piles produce a hard substrate capable of supporting a greater number and diversity of organisms than would naturally occur (Shinn, ref. 5). In two California studies, Turner (ref. 8) and Carlisle (ref. 9) concluded that the 20-foot high pile of cuttings beneath two oil platforms neither harmed nor benefited the marine community.

The myriad of encrusting forms that adhere to the hard substrate provided by the platform seem to be unaffected by the discharges. Barnacles not only live on and beneath the downpipe, but actually are attached inside the downpipe.

Fish have been observed swimming through the cutting discharge, some even taking cutting chips into their mouths, only to spit them back out upon finding them inedible.

Summary

The data as collected by Shell indicate that drilling discharges are rapidly dispersed and diluted in the water column. Data presented by Zingula, though collected at a different site, show the same effects. Of the parameters studied, only chromium was significantly above background levels. This was in mid- and bottom-water samples beneath the platform; however, these values were for total chromium, with no hexavalent chromium present in any of the samples.

Mr. Shinn has observed marine life beneath Gulf of Mexico platforms for many years and has noticed no detrimental effects. It was noted that platform structures were thickly covered with marine organisms. Barnacles were seen growing on and inside discharge pipes. Fish have been observed swimming through discharge materials with no observable ill effects.

The important questions to be answered are: What are the discharge components? What levels are present in the marine environment? What levels cause detrimental effects?

As a preliminary observation, it appears that harmful substances are being diluted far below toxic levels. Environmental observations seem to bear out the present hypothesis that the organisms are not affected by the drilling discharges.

Hopefully, input, such as elicited by this conference, will begin to assemble documentation on the effects that drilling muds and cuttings have on the marine environment.

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DISCUSSION

MR. JOSEPH G. MONTALVO (Gulf South Research Institute, New Orleans, Louisiana): I noticed in some of your data that you reported a higher level of chromium at mid-depth. I would like to add that in the GURC study we found a similar thing, and we attribute this to perhaps a high concentration of the microorganisms at the middle depths, and just below the water surface or at the sea bottom.

DR. ROBERT Y. GEORGE (University of North Carolina, Wilmington, North Carolina): I have a couple of comments and a question to Dr. Ray.

I think it is very interesting that the platform legs, the jackets, offer a new substratum in the offshore environment. One platform is 1 acre in terms of the subsurface area. So if there are 2,000 platforms, there is a 2,000-acre exposed subsurface area and we have a great deal of growth, as Dr. Ray pointed out and as we found in some of the studies in the Louisiana shelf.

The question is: When you have the drill cuttings added to the environment, does that offer a similar reef effect to the environment or do the drill cuttings basically remain bare?

And another question to Dr. Ray: At the outset you reported various levels in the mid-water, and bottom-water. Were these measurements made at the time drilling activity was going on?

DR. RAY: In answer to your first question, the drill cuttings would provide a reef-type substrate, but it depends on the area you are talking about. As has been observed in the Gulf of Mexico, these cutting piles dissipate fairly rapidly; also, they are being covered up. And this is why after a number of years they cannot find the cutting piles.

Now, I have read that in California--I believe it was the Santa Barbara channel area--that the cutting piles do seem to offer substrate, especially in some of the deeper water. Of course, on the Pacific coast, I do not believe that they are on a heavy sediment bottom like we are to start with. But in an area where they would not be covered up (the cutting piles), yes, they would provide a new hard substrate and probably start supporting a community like that.

Now, what was the second question again?

DR. GEORGE: The second question is: Was the monitoring done at the time of the drilling activity?

DR. RAY: Yes. They had been at this lime mud-base phase for several days prior to the sampling, and were continually drilling and discharging throughout the sampling period.

MR. CHARLES F. JELINEK (Food and Drug Administration, Washington, D.C.): You reported on some concentrations of total organic content, I think roughly between 5 and 15 parts per million. Were these above the background levels?

DR. RAY: The answer to that question is: I am not sure from the data I had what the background levels around that rig were. So I really cannot give you an intelligent answer on that question.

DR. STEPHEN P. MURRAY (Louisiana State University, Baton Rouge): It was very interesting to see some fresh new concentration numbers. I noticed on Mr. Shinn's slide that he had the location of the thermocline sketched in. This opens up another set of questions on optimizing the location of the downpipe, say, with respect to the thermocline. We are learning more about the coastal waters and their density gradients, both vertical and lateral. I really do not have a feel for how important the problem will be in the future--but if more work needs to be done in toxicity, certainly the location of the downpipe should be considered with respect to density gradients as far as maximizing the dilution rate. We know something about the thermocline at the base of the surface layer. But I think, from my experience, that it is a bad location; 30 or 40 feet down would tend to give you minimum mixing of the efflux as far as the suspended solids are concerned. Knowledge of the current fields would be of some assistance. We know that the tides have their maximums and so on; it might be more advantageous if we could concentrate discharges at certain times of the day, for example.

I have just one more comment. I was quite interested in the dilution model; mixing over the whole water depth that close to the rig is probably not realistic. Could you add something, perhaps, on the diffusion coefficient that was used? I rather suspect that this was the best looking picture available. You might say something about how that model was generated; that would be interesting.

DR. RAY: On your first comment, I do not have any background as to what would be the best discharge depths. If I remember from your comment, you are a physical oceanographer.

DR. MURRAY: Yes, I am.

DR. RAY: Suggestions and comments from people with your expertise would be very welcome on this question.

Now, to your second question, I will just beg ignorance, being a biologist, because I did not generate that formula and probably could not understand it if it were explained to me--as far as the way it was generated and run in the computer. But if you would like to have a little information about it, I will talk to you afterward and maybe we can provide you with the equation so you can have a better idea how it was generated.

DR. MURRAY: One more thing--the first few numbers that came out there looked interesting. We might also have to keep in mind the flow field that is induced around the rig as far as the sampling stations are concerned and the time-averaging of the samples. I have seen the high-altitude NASA shots where you see the Karman vortex developing. So you have got to know where you are sampling, and you could maximize your dilution rate by knowing where around the rig to put your downfall pipe to get into the main stream in order to maximize your diffusion coefficient.

DR. RAY: Your points are well taken. That is why I prefaced the paper with the words "preliminary study."

CHAIRMAN WENNEKENS: I would like to make one comment with respect to the thermocline and disposal of this material.

The material looks like it was relatively buoyant, it seems to be rising. So that means that if this is the case, you are going to introduce as much earth to settlement density interface. In your sampling, if you want to really look for where the material is, in terms of where the pollutants are, you should be very aware of the sampling at the interface of the thermocline. So, essentially, an arbitrary scattering of the sampling stations is maybe not representative of where the material actually is.

MR. JOHN R. JIMINEZ (EPA - New York): You have mentioned that some of these rigs are adding new species to the Gulf area. What I would like to know is, if you are introducing these species, are any studies being made or being contemplated to see what is the effect of these new species on the commercial fisheries along the Gulf Coast?

DR. RAY: I do not know. I misunderstood the original phrasing of your question. You made it sound like we are introducing new species; they are doing this all by themselves. Apparently, it is just a range extension. Recruitment can come from two different areas. One, of course, is the hard banks off of the coast of Texas, which are coral reefs. Secondly, we have the Gulf loop current which comes across the Yucatan coral reefs up through the Yucatan straits, and swings eastward through the Gulf.

At the present time, I do not know of any projects that are proposed to study what you are talking about. And, right now, the species that I have heard are present so far--the Caribbean types that they were talking about for the most part--are not in competition with the commercial species. A lot of the species that I was talking about are the small tropicals, and I do not know that they would pose a competition problem to the commercial species there.

MR. JIMINEZ: Yes. Even, as you said, when you put up a rig, the lower forms move in; eventually you will get the more complex forms.

My concern is that you eventually will get some type of predator into the area. And under a situation like this, some of the local fish might not be able to compete against the predators.

DR. RAY: Most of the large predators that come to my mind are already present there and have been there--for example, the grouper, jewfish, barracuda, the big pelagic forms such as the jacks, and mackerel. Offhand, I cannot think--I am thinking in generalities right now--of a species that would cause any problem there.

MR. JIMINEZ: This is the point I am really trying to make. It might look very beneficial to have these rigs out there. You have seen the beautiful commercials that some of the companies put out on TV showing how the rig is bringing in all of the new forms. That might not be a beneficial effect; that might be an adverse effect if the fish do replace commercial fish in the area.

CHAIRMAN WENNEKENS: I would like to make a comment on this. Probably, those things have always been there in the vicinity of the environment, except this is the first time we have had people to go see them because we have the rigs. I do not think it is unique as far as new species coming in. I think it is because there was never before anybody in the right place to observe them.

DR. MURRAY: It is interesting that the satellite work has shown that the loop current, as Dr. Ray just mentioned, is moving around. In the last few years it has tended to stay a little further north, and it seems to be going through cycles. I suspect this is probably what is happening because it is bringing up pure Caribbean water. We will probably see this for 3 or 4 years and then for 3 or 4 years it is going to stay down South.

MR. JAMES B. JOHNSTON (Bureau of Land Management, New Orleans, Louisiana): One study concerning offshore oil platforms and the Caribbean-type tropical fish being found there was conducted by some people at the University of Southwestern Louisiana--Farley Somaiya, Dick Josey, and Joyce Teerling. This paper has been accepted by "COPEIA"; it will be published in 1976. If you would like a copy, I imagine you could write to Dr. Josey. I will not get into the details of the paper, but I would like to point out that one study has been conducted concerning offshore oil platforms and the results will be incorporated in our Environmental Impact Statement number 41.

23 May 1975

Session IV:

RESPONSIBILITIES OF WELL DRILLERS

Albert J. Fritsch, Ph.D.[*]
Chairman

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[*] Director, Center for Science in the Public Interest, Washington, D.C.

SESSION INTRODUCTION

Albert J. Fritsch,
Session Chairman

Well, I would just like to say a few words at the beginning on the question of responsibilities of well drillers. Any person who works in the environment necessarily is tinkering with the natural world in which we live. Therefore, not only has he certain rights in working on this world but also certain responsibilities. And the responsibilities are sometimes forgotten.

Industry has tried to take care of its own problems, self-policing. I think that is the heart of the problem here, and is in any environmental area, any practice. Is this self-policing enough? Is the industry working as best it can? Does the public have a right to know what it is doing?

Do you know, we sat here for 3 days, and we finally were told that there are 200 proprietary compounds; we have no idea what they are. We know what some of them are, but even for those, we do not know how much is being used or where it is being used. Does the public not have that right to know?

These are questions that the public asks. The demands of the public clash with the demands of the industry to be self-policed. And this is the heart of the problem that brings us back this afternoon. How much should the government be able to regulate? How much can be done without the public knowing it or with the faith that it is being done properly. How long do we have to allow this to continue without knowing what is happening?

There may be no individual here who knows all that is happening, but the collection of a regulated industry will allow the government, at least, to know what is going on.

And so these are the questions that come before us. And I think those questions will be partly treated by the speakers that we have today.

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OBJECTIVES OF WELL-DRILLING REGULATIONS

Jay H. Lehr, Ph.D.*

Abstract

It became apparent to the National Water Well Association that the water well industry had no organized body of knowledge concerning recommended standards for well construction, and that the state-of-the-art in that industry lagged behind that of the oil well industry. The lack of systematic instructions for engineers at time led to inadequately constructed wells that created a channel through which surface water pollution could move down and pollute ground water.

The Federal Government was concerned with supplying technical information to aid the States in their enforcement of safe drinking water standards. Four years ago, the Environmental Protection (EPA) requested that the National Water Well Association develop a document on all the alternative methods of drilling sanitary and nonpolluting wells. Dr. Lehr and Michael Campbell directed 33 experts over 3 years and produced a state-of-the-art manual entitled Manual of Recommended Well Construction Standards.

Not a set of regulations, the document is rather a detailed instruction manual to guide home owners, engineers, industries, and municipalities as to the design specifications that would best fulfill both safety standards and the constraints of the particular building situation. The manual covers 17,000 possible kinds of wells, and is computerized--by feeding coded information about the type of well needed, a computer can respond with the construction procedures most appropriate for each well.

The document was submitted to EPA in May 1975, and is due to be published shortly.

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*Executive Director, National Well Water Association, Columbus, Ohio.

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INTRODUCTION

The National Water Well Association had been involved, to a certain extent, in the oil industry for about 8 years when we recognized that the advanced technology for well construction existed in the oil industry rather than in the water well industry. We felt that there was perhaps as much as a 10-year gap in technology transfer between what was developed in the oil fields and what eventually resulted in new techniques in water well construction.

We went to the Department of Interior's Office of Water Resources Research some 7 years ago and talked to them about a project to close that gap. The idea was to write a state-of-the-art report on well construction technology, utilizing primarily that technology developed in the oil industry that was transferable into the water well industry.

We worked for a period of 3 years to develop this state-of-the-art manuscript. It was eventually published as a textbook on water well technology jointly authored by Michael Campbell and myself. It was an initiative toward getting involved on a grass root level with what was going on in the oil well industry, and I think a most successful one. We at the National Water Well Association have continued since that time to stay in touch with what is going on in the oilfield, recognizing that this is where the research is done and where the money is spent to develop techniques. On a continuing contract with the Department of Interior's Water Resource Scientific Information Center, we have abstracted or attempted to abstract all of the world's literature in the area of water well construction. Still, the major area of technology is still coming from the oil industry.

The Environmental Protection Agency (EPA) recognized a few years ago that while there now may have existed a state-of-the-art report on water well construction technology, there did not exist a body of knowledge for engineers and industry individuals concerning actual specifications of properly constructing a water well so that it would meet the sanitary standards of various State regulations. EPA noticed further that there were tremendous problems in drawing up adequate specifications for water well construction because of that lack of a body of knowledge.

A body of knowledge clearly exists in the oil industry, where there are a variety of standard manuals and reference books that one can consult in determining how to properly design and construct an oil well. Similar reference material did not exist in the water well industry so that, by and large, specifications were entirely inadequate. Engineers did not have a proper feeling for the development of design criteria for a well.

This has led, in the past, to the construction of wells that were often either too expensive for the needs or too inexpensive. The latter were inadequate from a sanitary standpoint, leading to pollution, and the former were more than adequate, leading to an economic waste factor.

EPA came to the National Water Well Association research facility some 4 years ago and asked that we put together a national committee of experts on well construction to develop a manual of recommended standards for well construction.

The committee consisted of 33 individuals, nationally, who worked over a period of 3 years. The 33 were made up of 11 ground-water hydrologists, geologists, and engineers, and 22 individuals in well construction as contractors, manufacturers, or the like.

The committee gathered together information on all the alternative ways that one can design a water well in a manner that will be nonpolluting and sanitary.

The document has been reviewed by better than 200 people in literally all endeavors that touch on water supply and pollution control, and generally, well construction technology.

The document that would guide people into proper well construction was not intended by EPA to be of regulatory nature. It was never the design of EPA to develop a document about which they would say, "This will be Federal law," or, "This should become State law." Rather, it was the beginning of a concept that I think is spreading within the

Federal Government today, certainly at the EPA level. That concept is that it is the duty of the Federal Government to support the population, and especially the State governments, in providing technical knowledge to help the States do the job that they know needs to be done. In the area of environmental protection, the Government in theory should protect all of our natural resources, whether they be air or water.

I think the development of this manual has led to something of a model for other projects that are currently going on in the Environmental Protection Agency. Some of these I can describe from firsthand knowledge.

I am a member of the National Drinking Water Advisory Council, which is a 15-member body set up under the Safe Drinking Water Act. The Council advises the EPA on the implementation of this act, which was signed into law on the seventeenth day of December, 1974. The subject of ground water protection is only rarely mentioned in the Water Pollution Control Act of 1972, Public Law 92-500, which allows the Federal Government little or no jurisdiction in the regulation of ground water pollution. Perhaps this is a very good thing because the implementation of 92-500 has not largely been successful. The Federal Government has taken a rather heavy-handed approach in telling the States what they must do, and it has gotten a backlash so that not yet half of the States have accepted the Federal Government's primacy in the regulation of our surface waters under that act.

The fact that undergound water is not mentioned or regulated by the Water Pollution Control Act of 1972 is certainly due to the effort of the oil and gas industries to keep it out of the law. It is not secret that they lobbied against it, not necessarily because they felt it would stop them from doing things that they were already doing. They lobbied against it, and probably rightfully so, because they recognized it would place a tremendous amount of red tape regulation on them and require them to be reporting and doing many things that would not make their product better nor their operation safer but which would cause them undue cost and inconvenience. So they opposed it on this ground.

As 92-500 worked out, it did cause a lot of people, a lot of companies, and the country itself, that kind of trouble. And it is questionable how successful it has been considering the trouble that it has caused.

The Environmental Protection Agency has learned from these mistakes, I feel, and plans to implement the Safe Drinking Water Act of 1974 in a far more diplomatic way; at least all indications are pointing in that direction. The Safe Drinking Water Act has picked up and filled a void that existed in the Water Pollution Control Act. It does give the Federal Government jurisdiction for the regulation of underground water. Section C of the act is the Underground Source section, which gives the Federal Government jurisdiction to regulate a wide variety of underground water pollution.

The language of the 1974 bill was initially addressed to things like deep well injection, but it broadly speaks to the development of programs for the protection of our underground water by all States in a very broad manner. EPA interpreted, and I think very correctly, that it was the intention of Congress to cause the States to begin addressing the ground water pollution problems and to regulate them. But in saying, "Cause to direct, focus attention and regulate," they are this time choosing not to tell the States how to do it, not to set out a by-the-numbers approach, but rather to give the States the impetus and the direction to do what they want to do in a manner that they choose themselves--a very flexible approach.

For instance, under this bill, there was talk at one time that the Federal Government would lay down standards about regulating the reinjection of brine waters as a potential pollutant.

Happily, a sentence was placed in the bill that made it clear that any regulation of reinjection of brine should be done only if it were clear that doing such was going to pollute an existing or potential drinking water supply. So clearly the bill stated that it was not to become an obstacle to the development of energy. But beyond that, when it came time to begin developing regulations on potential underground pollution, such as brine reinjection, pits, and waste lagoons, the Federal Government decided that it would utilize a concept of regulation called "Regulation by Rule" versus "Regulation by Permit."

When the Federal Government regulates something by rule, it is first establishing that, in fact, it has the jursidiction over the regulation. It is saying that the States must regulate something, but it does not tell the States how to regulate it. Broadly speaking it says, "The States must address the subject, determine what their problem is, what their resources are to manage it, and then establish regulations that are manageable within the context of the nature of their problem and their resources to handle them."

The Federal Government maintains a review process but makes it very clear that this is to be of a very loose nature, and it will be simply an overseeing in a helpful manner rather than a regulatory manner. It appears that this is the way the Safe Drinking Water Act and the Underground Protection Section are going to be handled. At last the Federal Government has allowed the people to govern themselves. The States will address their problems individually and implement them, but the Federal Government will be providing a number of resources. They will provide research, reference documents, and material, looking at the collective problems of the States. They will give the people in the States the impetus to go to their decisionmakers and their legislators and say, "Look, the Government has asked us do this; you have got to give us the resources and support us in doing it." So we think that it is going to be a cooperative program.

Let us return to what I think has been something of a model to this approach. Four years ago the EPA decided that it wanted to produce a document that would help the States determine how wells should be constructed. Ultimately, we have produced a manual of recommended well construction standards. Again, the document was not meant to be Federal law; it was not meant to be State law; it was meant to be a reference book for the States so that they can decide what kind of regulations they want.

We know that the construction of water wells is a major source of ground-water pollution. Inadequately constructed water wells create a channel for surface water pollution to move down into a well and pollute the ground water. Unless the wells are constructed properly, it creates a transfer zone for unpotable ground waters to move into zones of potable ground waters. We feel in the water well industry, therefore, that we are, indeed, our own worst enemy. Unless we regulate the construction of well drilling by at least having educational material that will show well drillers, home owners, municipalities, industries, and engineers how they can specify the construction of wells under a variety of criteria that will result in the sanitary construction of a well, we will continue to inadvertently pollute our ground waters through inadequate operations, and give ground water a bad name. So it is certainly a motherhood and apple pie situation for us to want to seek proper education as to how to do things correctly.

When the EPA first said it was not looking for a law but rather for guidelines, we did not trust it. When it said it was not looking for something to make law, and then drew from the industry to get the experts to do the job, there was still a tremendous degree of distrust.

So we decided to develop a document that could not conceivably be made into a law. We planned to develop a document that would be simple to use but too complex to write into law. We told EPA that we were going to do that.

Recently I was giving a talk about the new look of EPA. (I really believe there is a new look, although we need safeguards. We have to stay awake at the switch and help it at every turn.)

A fellow told me a story that summed up this approach. Two fellows were walking in to see a John Wayne western movie. And one of them, before he walked in to the movie, said, "You know, this is a John Wayne movie; there is going to be a lot of horseback riding, there is going to be a chase." He said, "I bet you 10 bucks in the first 30 minutes of the movie John Wayne is knocked off his horse." And the other guy said, "You are on, and I will bet you that he does not get knocked off his horse."

And so they go in. In about 18 minutes into the movie, sure enough John Wayne is knocked off his horse. And the guy who lost the bet immediately took out his wallet, took out a 10 dollar bill and handed it to the fellow who said he would get knocked off of the horse.

The guy who said he would get knocked off his horse said, "You know, I really cannot take this money from you because I have to make a confession. I already saw the movie. I knew he was going to get knocked off the horse."

The guy who handed him the money said, "That is okay, I already saw the movie, too."

Well, the guy who won the bet said, then, "Why in the hell did you bet that he would not get knocked off the horse?"

He said, "Well, I though maybe this time he would know better."

It is the same kind of idea as we look with trepidation at what EPA is doing. We hope for the best, but we are always afraid, really, that it is going to be a rerun of the same movie.

Let me tell you what we did regarding this document. The manuscript which was turned in to EPA around May 2nd--just a few weeks ago--will be published as the Manual of Recommended Well Construction Standards by EPA hopefully within the next 90 days. There has been such a call for the manuscript that we have threatened (if they do not publish it in 90 days) to obtain through legal means the right to publish it and to put it out ourselves, because the product has obtained a lot of attention and people want it.

In the document, we figured out that there are a lot of different ways of drilling a well, and that the way you drill a well, from a sanitary standpoint, depends on what the well is going to be for. The credit for this rather ingenious system goes to Robert Heater of North Carolina, who is to a certain extent the father to this manual. We developed a system of alternate regulations, wherein, with certain criteria or certain descriptive words about what the well is going to be used for and how it is going to be drilled, you can derive the minimum standards.

This manual contains directions to build 17,000 different kinds of water wells. Again, that is why I say it is very hard to turn it into a regulation or a law--because there are 17,000 combinations and permutations. (In fact, about 15,000 of the 17,000 solutions duplicate each other, so there really are not that many ways.) The document does lend itself to being computerized--that was part of our design--but it is also a very simple manual.

In constructing a well there are many things we do. We drill test holes, we log, and we sample. We develop specific well construction procedures. We select well casing and install the well casing in a variety of ways. We grout the well a variety of ways. For well filter construction, we either have a natural gravel pack or an artificial gravel pack. We align and plumb the well in certain ways. We develop the well in a wide variety of ways. We test the well for its performance. We disinfect the well by several means. We take well samples and analyze them in many ways. And we abandon the well in a variety of ways.

For each of these broad subject categories there are many subtasks required to fulfill that particular part of the project. And for each one of these subtasks there are numerous ways to do it. How do you decide which is the best method?

You could always do it the most expensive way or the most stringent way, but frequently that would waste both time and money. The decision depends on what kind of a well you are drilling.

We immediately started out to collect all of the alternative procedures used in the various aspects of constructing a well. We collected them into subject areas and then put them in order, from the simplest to the most complex, and from the most careful to the least careful (the least careful may be good enough sometimes).

Then we determined how to define a well, and how to define the different ways to go about constructing them. The purpose of the well will have a bearing on how you perform the subtasks mentioned earlier. The well may be an irrigation well, a domestic well, a municipal well, a commerical-industrial well. It may be for exploration, for processing water, cooling water, or dewatering. It may be for geothermal mining, solution mining, or mining brine water or minerals. Or it may be a recharge well, a drainage well, a waste disposal well, or a test well.

Your choice of construction methods also depends upon how much water you hope to get out of the well. We have definitions for high-yield well, a low-yield well, and a medium-yield well. In addition the character of the interval you penetrate on the way down to your producing zone will affect your selection of methods. Different procedures are required for drilling through unconsolidated material, consolidated, unstable-consolidated, or a combination of materials.

Similarly, the character of the producing zone--whether it is consolidated, or not consolidated, unstable-consolidated, or a combination of both--affects the choice.

The method of construction, assuming you have a choice, is going to influence the handling of subtasks. You may drive the well, auger it, jet it, or drill a cable tool well. You may use a rotary system with conventional fluid air circulation, a reverse hydraulic method, or a combination of drilling and driving.

And finally, strangely enough, the way you pay for the well is going to affect certain things you do. You may pay in a lump sum, drill for time and materials, or use a unit price.

We came up with what we think is a very ingenious chart. The chart lists the well criteria that I just cited down one side, and it lists all of the types of functions that we do down the other side. Then there is a tremendous grid pattern. In all of the grid patterns there are numbers, although most of them are zeros (and zero means that it does not matter).

This is how the chart works. Imagine how you pay for a well, for example. It affects some, but not all of the things, so you put in a zero. Where it does have an effect, and where therefore you think that a certain function should be done a certain way, you look into the book. There you find that under certain conditions you grout a well one way, and under other conditions you should grout it a different way. There is a very simple key that guides you through this big raft of numbers.

I would imagine that the effective utilization of this manuscript for writing criteria for specifications in construction of a well would take about 2 hours in intensive study. And I could make people expert in the utilization of this manuscript in a 2-hour workshop, although it is a self-taught text, so that you do not really need personal instruction.

The document then consists of two parts. The first is the chart, which we call the master key to the Water Well Standard. That unlocks the door to the manual. The second is the book itself, which is a manual of well construction standards. We hope that in this book there are entries to describe every single way to perform any function used in drilling a well. That is a very broad statement. But all told, 200 people worked on this document for 3 years. And I think they were really scratching their heads to come up with new things. I do not think we missed too much.

So we have a manual of all of the ways you do everything. But the manual is in a sequential order; there are instructions as to how to go in the manual to get out your kind of well specifications.

If you define a well, early in the manuscript we have sample worksheets, strange looking charts, that show you how to pull the right material out of the book. And then there are sample problems worked on how to go through it.

In our sample we use a well, called a CKLPX1Z. There is only one minimum way to build a CKLPX1Z well. You can see how easily this is going to work. When this all goes into a computer, someday, when we talk EPA into some more money for programming it (it is really pre-programmed), you would punch into a typewriter CKLPX1Z and out would print your minimum well construction standards.

When you go through the book, you do not have to use the minimum. At any one of your stopping points you could decide to do something better if you wanted. That is the way it is geared up.

For your information, what is the sample? C is a municipal well. K is a design capacity of over 100 gallons a minute. L is unconsolidated overburden. And P is unconsolidated producing zone. X.1 is a conventional fluid rotary method, and Z is the method of payment, which is time and materials. And you go in and you come out with the proper standard for that well.

We hope that this manuscript will be distributed to engineers, drilling contractors, and industries and municipalities all over the country as a guide, a book they can use to find a standard by which to find a specification. Believe me, there is a need. I have been in this job for 8 years, and rarely a week goes by that people do not call in for some information on writing a specification. We have got a lot of good engineers around who do not know how to write a well specification, and they are crying for something like this.

I think I have told you enough to know that you cannot take a document like this and turn it into law. But it is a document that EPA is going to publish and release because that is what the Government is supposed to do; it is supposed to provide us with reference material to do the job we all know needs doing, and that is the protection of our underground water. There is nobody that opposes that. But we sure oppose being told what to do by the numbers, by people who often know a good deal less about the subject than we do.

DISCUSSION

MR. OLLIS SMITH (State of Tennessee, Division of Water Resources, Nashville, Tennessee): How does the Safe Drinking Water Act apply to the individual water well?

DR. LEHR: Broadly speaking, the EPA is taking a position that the intention of Congress is to control the pollution of well injection systems.

Broadly defining a well injection system, we can be talking about other than conventional wells. We could be talking about pits and lagoons, and anything that puts something into the ground. And while that is a strange definition, they will not get any argument if they do not attempt to use it in a forceful manner but simply say, "Hey, get out there and look at your problem."

But a water well, is, indeed, a well injection system, although it is not thought of that way. We drill a water well to get water out but clearly things go back in. If it is improperly constructed we have pollution moving down the side of the casing and into the ground. So it can, I think, usually be held up in Court that the construction of a well can be a well injection system. There is the regulatory potential, but no intention whatsoever to use it.

In a ground water protection program that the State will hopefully develop under this law, one of the things that they certainly should be doing is regulating the construction of wells in their State, however they want to do it. You know in the State of Tennessee what your problems are, what your resources are, and what kind of a solution will be best accepted. It will be up to you and those in your State agencies and with your State Legislature to determine how loosely or how strictly you want to enforce it.

So the answer to the question is, the Safe Drinking Water Act does, indeed, have an effect on the individual wells from the standpoint of protecting ground water but the extent of that effect is going to be determined not by the Federal Government but by the States.

MR. SMITH: Who decides if you are complying to the standard?

DR. LEHR: That is almost a question I do not want to tackle because the attitude now is, "Look, we have all wanted to do the right thing and nobody is going to hit you over the head if you do not do it the way I want you to do it."

The question really is, "If you set up regulations and then you show them to the Federal Government and it thinks they are too loose, what is it going to do to you to make you do it tougher?"

I am saying they are not going to do anything, if within reason you approach your problems in an intelligent way.

That is a very idealistic approach. "Who is he kidding?" you are saying. Are they going to come out with the standard old blackjack they have been using for years?

Well, I am telling you, they just do not have it anymore. They are tired, they are beaten, and they are worn out, and for the first time they are going to start using diplomacy, they are recognizing that the intelligence is at the State level, and that they are not dealing with children, and they are going to do the job the way it should be done.

So the answer to that question is, if you are being straight with them, they are going to be straight with you.

MR. SMITH: I am for States' rights and that is fine. But sometimes we find in Tennessee, unless somebody tells us on Federal level, that the legislature says, "Well, we do not have the money to do it." You know how this goes.

DR. LEHR: We have analyzed this problem philosophically, and we have used the surface water problem as a model--that is ORSANCO, the Ohio River Sanitary Compact. Over about a 12-year span, the industry working on the Ohio River voluntarily employed pollution control measures to improve its effluent flow into the river. By sitting down in an intelligent manner, discussing the problem, 75 percent of the industry fell in line and dramatic results were done on the Ohio River. Twenty-five percent of the people did not fall in line or begin to fall in line until the Water Pollution Control Act of 1972. And I think that is about where we are at. I think 75 percent of the guys are good guys and they will do it with just a little gentle persuasion, and 25 percent of them are eventually going to need the blackjack.

Tennessee might be one of those States. I hope not.

But at such time when most of the States are being reasonable, and their legislators are doing what needs to be done, we will get 75 percent of the job done. Twenty-five percent will be undone. At that point, though, that 25 percent will have no friends. And that is when I think specific enforcement regulations, you know, in terms of bringing power to bear on them, will be worked out in more detail.

MR. SMITH: I hope you are right.

In Tennessee and elsewhere, I wonder about some of the compliance without the blackjack.

One other thing, I assume that much of the funds, if there are funds available for the enforcement of this act, will go to the health agencies in the various States. Are you aware of what the plan is on that?

DR. LEHR: Yes. There is currently too little money available. I have spoken in the last 8 days to both the House Appropriations Committee and the Senate Appropriations Committee on the EPA budget. OMB recommended next to nothing, which is what OMB is supposed to do--"to recommend against anything except the Defense Department resettling Vietnamese refugees."

Russell Train went over and knocked on the door of the White House and sat down with President Ford and talked the President into putting up $10 million in his budget for State grant programs, with essentially few if any strings attached. Seven-and-a-half million dollars of this are for what we call the Tap Water Program and $2-1/2 million are for the development of the Ground Water Program. This spreads itself very thin, you know, when you divide it up between 50 States and five territories.

So I presented a case to Congressman Bolin's House committee on the EPA Budget, and to Senator Proxmire just 2 days ago. He almost laughed when I came in talking about $2-1/2 million since the guy before me was begging for $3.95 billion for HUD and Urban Renewal. The same committee looks at HUD and EPA. And so I had very little difficulty getting a fairly strong rapport on the problem. And we are hopeful that increased sums will be provided.

The States are going to have to get together themselves to decide who gets the funding. The bill does not say it goes to the Health Department, it does not say it goes to the EPA. The State agencies are going to have to work together in deciding what agencies are going to control this.

EPA has also sponsored another intelligent project of this nature, which will be completed sometime this fall. It deals, to a certain extent, with the institutional problem of how the State could design a program using the current resources of its State EPA and State Health Department to design a ground water protection program--not a new super agency, not a lot of new people, but using its present resources. There has to be a planning group to decide how to utilize the money the Federal Government will give them.

MR. GEORGE H. HOLLIDAY (Shell Oil Company, Houston, Texas): What are the objectives of oil well drilling or well drilling regulations? I am lost.

DR. LEHR: I thought I said that in the first sentence.

The objective of water well drilling regulations is to produce wells that do not pollute our underground water resources.

MR. HOLLIDAY: Thank you.

DR. LEHR: One last point. In putting out all of this optimism, and I know I come off an idealist, I always end up by quoting Pascal's wager. If you recall, Pascal wagered that there was a God. The reason being that if there were not a God, it did not matter, and if there were a God, he would get into heaven.

I am betting on EPA, because if I am wrong, you know, we will just go on the way we are, and we will have lost a little good will and good intentions. But if I am right, maybe we are all gearing ourselves up for a cooperative venture which will make the management of our environment far better tomorrow.

RESPONSIBILITIES OF OFFSHORE DRILLING REGULATIONS

Donald W. Solanas*

Abstract

The Federal Government, with the passage of the Mineral Leasing Act in 1920, allowed the leasing of areas on the continental United States for oil and gas exploration and production. At that time, the U.S. Geological Survey, a scientific branch of the Federal Government, was delegated supervision and regulation authority of drilling and producing operations.

In 1953, the Outer Continental Shelf Lands Act provided that the people of the United States (Federal Government) owned the sea bottoms off the continental United States. After considerable dispute between the States and the Federal Government as to jurisdiction and leasing authority, the Submerged Lands Act gave a certain portion of the Continental Shelf to the coastal States. The Federal Government has jurisdiction over those areas not given to the States. It was thus in 1953 that the U.S. Geological Survey began to regulate Outer Continental Shelf oil and gas drilling and producing operations.

The organization consists mainly of scientists--petroleum engineers, geologists, geophysicists, biologists, oceanographers, etc. Attention is concentrated in the Gulf of Mexico, where there are presently approximately 6,000 producing oil and gas wells. The responsibility for safe operation of these sites, however, lies not only with the regulators, but principally with the lessees of the offshore lands.

The U.S. Geological Survey has an involved, regulatory role in well drilling operations. We have authority, in supervising and inspecting operations offshore, to shut down operations that are not being conducted according to the rules and regulations, or are causing harm to the environment. And, of course, if an operator does violate a rule, regulation, or order offshore willfully and knowingly, he can be taken to Federal court and be fined. You might say that we do not take the idealistic attitude that everyone is going to do right all the time on every operation in the Gulf of Mexico.

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I would like to discuss the Outer Continental Shelf, what is going on there, just what we, as a Federal agency, do to supervise and regulate. (I have prepared some literature on this topic for you to take with you. As an example, see attachment A, Update - Outer Continental Shelf Lease Management Program.)

The Continental Shelf is that part of the continental United States that is submerged by water. The Continental Shelf begins at the seashore and runs out to approximately 600 feet of water depth, and from there it slopes more rapidly to a depth of 1,800 feet or 600 meters; this is called the slope.

Supervision of oil and gas operations by the U.S. Geological Survey commenced around 1920 by the passage of the Mineral Leasing Act of 1920, which permitted operations to be conducted for oil and gas exploration and production on Federal lands within the continental limits of the United States in practically all of the States, but principally in the States west of the Mississippi River. At that time, Congress decided that the U.S. Geological Survey (being one of the few scientific agencies of the Federal Government), Department of the Interior, should have the jurisdiction of representing the Government and the people of the United States to see that these public lands were operated in a safe manner.

So in 1920 this organization began with petroleum engineers and petroleum geologists to supervise onshore leases. This has gone forward and is still proceeding today.

In 1953, the Outer Continental Shelf Lands Act was passed, principally as a result of President Truman's proclamation in 1945 that the Federal Government, or the people of the United States, owned the sea bottoms off of the continental United States.

At first there was quite a contest as to whether the States would have jurisdiction and leasing authority on what the President proclaimed as being owned by the United States. This dispute journeyed through the legal process and to the Supreme Court. The Supreme Court determined that the States owned only those lands inside the State boundaries and that the Federal Government owned this newly proclaimed land on the Continental Shelf.

The States did not like this one bit. They protested and they complained; they went to court and to Congress. In early 1953, the Congress passed the Submerged Lands Act, which gave back to the States, or gave to the States, a portion of the Continental Shelf. It gave to the States that border the oceans and the Gulf of Mexico out to 3 miles offshore. It gave to the State of Texas out to 3 leagues; it gave to Florida a strip of the Continental Shelf on the Gulf side of Florida out to 10-1/2 miles (3 leagues).

In 1953 Congress also passed the Outer Continental Shelf Lands Act, which set into motion the Federal jurisdiction and Federal control or supervision of leases to be sold and issued. So, as to offshore operation supervision by my organization, we began to function in 1953 on the passage of that Act.

The legal act and the oil and gas regulations promulgated by the Department of the Interior are in this "blue" book. I am sorry that the shipment of copies of this book did not arrive for me to have them available for each of you. It is the forerunner to the OCS orders, which are the implementation of the general regulations. If any of you would like a copy of this "blue" book, which is called Oil and Gas Regulations, there is a stamped address on the copy of the OCS Orders book that you may have picked up; please write, and I will be happy, when the supply comes in, to send you a copy.

As of today the USGS has a large operation in the Gulf of Mexico, principally because that has been where most of the oil and gas exploratory and development operations have been conducted off of the United States.

Our regional organization, which is headquartered in Metairie, Louisiana, on the outskirts of New Orleans, today employs approximately 330 people, most of whom are scientific types: petroleum engineers, geologists, geophysicists, petroleum engineering technicians, oceanographers, marine biologists, chemical engineers, civil engineers, mechanical engineers, and electrical engineers. We have the whole suite of technical support that we believe is necessary to scientifically or professionally supervise this big operation in the Gulf of Mexico.

There are five district offices and three suboffices along the Gulf of Mexico. Operations that are conducted in the Gulf of Mexico extend from offshore Tampa, Florida, all the way to offshore Corpus Christi. Our field offices, our district offices, are located at Tampa and Panama City, Florida; New Orleans, Houma, Lake Charles, and Lafayette, Louisiana; Freeport, Texas; and, by this summer, in Corpus Christi, Texas.

We have 43 petroleum inspectors, whose job it is to be in the Gulf of Mexico 7 days a week, 365 days a year, to inspect the operations that are being conducted by the Federal lessees.

Twelve helicopters are permanently chartered, which operate daily, transporting our engineers and inspectors offshore to see that the regulations, requirements, and the permits of approval are being adhered to by the operators of these Federal leases.

I would like to present a few statistics to show the order of magnitude of the operation. There are approximately 1,500 effective oil and gas leases in the Gulf of Mexico. These leases extend from offshore Florida all the way to the Mexican border and begin at the 3-mile line or 10-1/2-mile line, depending on which State you offset, and go out to as far as 125 miles in the Gulf of Mexico.

Some 15,000 wells have been drilled in the Gulf of Mexico over the past 25 years. At present, there are some 6,000 producing oil and gas wells and 2,000 platforms on which there are producing oil and gas wells.

On any day that you may fly over the Gulf of Mexico and would make a survey, you would find that there are approximately 90 drilling rigs that are drilling wells on the Federal OCS.

I hope I have implied to you, if not stated, that the responsibilities of offshore drilling operations lie not only with the people who supervise the operation, but principally with the Federal lessees or the operators of the leases offshore.

What a change there has been in the offshore petroleum operation over the past 20 years. Keep questioning things that are being taken for granted. This turns up many, many realities and causes many new solutions to be developed, many new technologies to be looked into, and the state-of-the-art continues to progress; all of this is well and good.

We are working in a very challenging industry; the energy industry is a very necessary industry. There is abundant energy in the North American Continent, in the United States and Canada. Undoubtedly, we are never going to run out of "energy." The energy is in the ground, and there is plenty of it.

True, we are rapidly using the liquid and gaseous petroleum energies, but there are other forms of energy that are in abundant supply. We are going to have to develop the technology, whatever the price is, to tap these sources of energy some time in the future.

DISCUSSION

MR. DENNIS G. WRIGHT (Environment Canada, Winnepeg, Manitoba, Canada): I have a few comments. Over the past 3 days I have been here, I have become aware that there are no regulations in the disposal of drilling wastes to the environment other than that the cuttings must be free of oils. And I would like to give you a bit of background in the Canadian experience, things that we have been doing.

For the past 2 years, Environment Canada, the Department of Indian Affairs and Northern Development, and the Arctic Petroleum Operators Association have been looking at the impact of the disposal of drilling fluids in the Canadian Arctic. We are about to come up with a set of guidelines that we think is very realistic and easily met. Rather than have the Government work by itself and come up with a set of guidelines, we have asked industry to cooperate with us to get something that is very realistic.

We started looking at the whole drilling muds and doing bioassays on them. We found they were acutely toxic to fish. But putting a rainbow trout in a drilling fluid was not really very realistic. Trout just do not live in mud.

In regulating what comes out of the well and into the environment, we are taking the approach that it is best to regulate the components that go into the mud. So we have undertaken a toxicity-testing program of all of the individual components that are used right now in Canada, in the Arctic. There are about 66 different components. Of these we have tested about 40 or so. And we have come up with a ranking. We have taken the different product categories--lignosulfonates, weighting agents, gelants, and things like these. Our philosophy has been that if there are X many components that do virtually the same job, you can take the one that is the least toxic, has the least potential damage to the environment, and put that into drilling mud. We would thus have a mixture of the least number of toxic components, so you will get the least amount of toxicity coming out.

We think this is a very sound approach and one that is very realistic.

Our other approach has been to look at the volumes that have been produced. We have become aware that, until we did this, the operators really did not know how much mud was being wasted. And after a couple of monitoring studies, they became aware that it was virtually a one for one ratio, one barrel of mud per one foot of hole.

Now, in the Gulf of Mexico, this might not be much when you compare the silt load that comes down the Mississippi. But in some of the Arctic areas, both on the East and West coasts of Canada and the States and in the Arctic areas, the siltation can be a problem.

So we are asking the operators to cut down, if they possibly can, on the volume of their discharges.

We heard a lecture on solids equipment, and I think that, if we can continue to work in this area, we can possibly reduce the volumes that are produced, perhaps down to, say, 900 to 1,000 barrels--to whatever is in the active mud tanks in the system.

As I say, our approach is to basically limit what goes into the mud and limit the volume. I hope this is a realistic approach, and I hope that the people in the States can learn from our experiences.

CHAIRMAN FRITSCH: This is a very good working principle, another working principle that we have.

MR. JOSEPH G. MONTALVO (Gulf South Research Institute, New Orleans, Louisiana): My research group is involved in the analytical chemistry of drilling muds and the drill cuttings contained in the muds. I think if we are going to direct our future research efforts to meeting the regulations, I would appreciate it if you could tell us what are the regulations regarding this disposal offshore of oil-base and water-base muds and the cuttings contained in them, if that is possible.

MR. SOLANAS: I think we have touched on those points in the comments and presentations that have been made by the people here that have been with the research groups and with the supply groups. I believe the question has been answered in the comments that I have made, that no oil-base muds are allowed offshore except under the special stipulations and conditions. And you cannot dump oil-base muds into the Gulf of Mexico. Our regulations do not allow a lessee to dump anything into the Gulf of Mexico except what came from "Mother Earth" in the first place--that being the drill cuttings, the ground-up earth in the borehole. Nothing else is allowed back into the Gulf of Mexico unless it is clean and can be pumped back into the Gulf without harming the aquatic life or human life there.

We do not have a specific manual of dumping regulations or principles on this subject. This is an ever-changing technology. What you use to drill a well off of Tampa, Florida, is a lot different than what you use in a well off of Corpus Christi, Texas.

MR. JOHN R. JIMINEZ (EPA - New York): I would like to know what the reason for having the so-called new regulations for OCS for oil and gas drilling is? We received an impact statement a few weeks ago. I would like to know what the reasons for having the new rules are and what the main difference between these new ones and the old ones are?

MR. SOLANAS: I am not familiar with the specifics of your question as to what new rules you received and where they apply, whether you are talking about the Gulf of Mexico or whether you are talking about the Atlantic or elsewhere.

MR. JIMINEZ: These are just general rules. This came out in an impact statement released by the USGS May 2nd.

MR. SOLANAS: Well, the USGS does not release environmental impact statements on drilling rules. It may be something that you read that the Bureau of Land Management released.

MR. JIMINEZ: No. This is the USGS, I am positive of that. I have a copy upstairs in my hotel room.

MR. SOLANAS: Rules that are in an environmental impact statement released by the USGS?

MR. JIMINEZ: It was in an environmental impact statement written by the USGS on what they call new regulations for OCS drilling for oil and gas.

MR. SOLANAS: I do not believe I am that ignorant of what the USGS has done. And I do not want to disagree with you. It must be something else somewhere other than the Gulf of Mexico, but maybe we can talk about it after this presentation, and you can pin it down for me, and I can look into it and possibly get back and communicate with you as to just what this is all about.

MR. JIMINEZ: Okay. I do have the document upstairs. I am reviewing it presently. The main reason I asked is because the statement itself does not pinpoint the differences between two regulations; it just discusses the new ones and says that the old ones will just not apply anymore.

MR. SOLANAS: That quite surprises me. We are going to have to look into that, you and I.

REGULATION OF ONSHORE AND OFFSHORE OILFIELD WASTE DISPOSAL

James E. Smith*

Abstract

The Texas Railroad Commission regulatory rules and statutes that control the disposal of waste which occurs from oil and gas operations in the State is reviewed. A brief history of waste disposal regulation as it has been developed over the years is presented. The present status of waste disposal operations as well as the inspection and enforcement practices of the Commission is reviewed. How these waste disposal rules and regulatory practices relate to the specific case of drilling fluid disposal is discussed.

The Texas Railroad Commission, an agency of the State of Texas, has the responsibility for the regulation of waste disposal on both State lands and State waters. The types of waste disposal from oil and gas operations may be classified as follows:

1. Produced salt water and brines,
2. Hydrocarbon wastes,
3. Solid waste,
4. Drilling and workover fluids,
5. Other miscellaneous waste.

General Responsibility

Both through its broad authorization and through specific legislation, the Railroad Commission of Texas either bears or shares the responsibility for preventing, eliminating, abating, or remedying the pollution or contamination of freshwater supplies, either surface or subsurface, by brines, mineralized waters, or hydrocarbons, encountered, produced, or released in conjunction with the exploration for or production of the hydrocarbon resources of the State of Texas.

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In broad categories, this authorization involves:

1. Protection of freshwaters during the drilling of exploratory wells,
2. Protection of freshwaters during production of oil or gas wells,
3. Protection of freshwaters after abandonment of wells, either exploratory wells or "dry holes."

The exercise of these responsibilities is made under general statutory authority, statewide rules, or special orders.

Statutory Authorizations

1. Texas Constitution Article 16, Section 59(a) - This constitutional amendment is the basic authorization for the Railroad Commission's jurisdiction, declaring the conservation and development of the natural resources of the State, specifically including water, to be public rights and duties.
2. Article 6004 - One of the first statutes pertaining to oil and gas operations (Acts of 1899) requires the casing of wells to exclude all surface or freshwater from the oil- or gas-bearing rock.
3. Article 6005 - The second of the first group of statutes required the proper plugging of wells drilled for oil and gas. This statute was amended in 1965 to give the Commission more detailed authority for the requirement of plugging abandoned wells, and fixed the liability for the cost of such pluggings in instances where the normally responsible parties are either unavailable or insolvent.
4. Article 6008, Section 6 - Authorization to make and enforce rules, regulations, and orders to...require dry or abandoned wells to be plugged in such way as to confine natural gas and water in the strata in which they are found, and to prevent them from escaping into other strata.
5. Article 6029a - Authorizes the Railroad Commission to make and enforce rules, regulations, and orders in connection with the

drilling of exploratory wells, and wells for oil or gas or any purpose in connection therewith, production of oil or gas, and the operation abandonment, and proper plugging of such wells to prevent the pollution of the streams and public bodies of the surface water in the State, and any subsurface water strata that are capable of producing water suitable for domestic or livestock use, or for irrigation of crops, or for industrial use, which would result, or might result from the escape or release of crude petroleum oil, saltwater, or other mineralized waters from any such well or from operations in connection therewith.

6. Article 6029b - Effective on August 28, 1967, gives the Commission supervisory control and regulation of the transportation of saltwater and other oilfield brines by tank trucks, including the requirement for license and identification of vehicle.
7. Article 6046 - Authorization for the Commission to make and enforce either general rules, or rules applicable to particular oilfields.
8. Article 7621d, Section 10(c)(4) - This article places sole responsibility on the Railroad Commission of Texas for the control or disposition of waste, and abatement and prevention of pollution of water, both surface and subsurface, resulting from activities associated with the exploration, development, or production of oil or gas.
9. Article 7621b, Section 2a - Requires permission from the Commission before drilling an injection well, or converting an existing well into an injection well, for the purpose of disposing of saltwater or other waste rising out of, or incidental to, drilling for or producing oil or gas.

Commission Rules

1. Rules of Statewide Application
    a. Rule 7 - Requires that hydrocarbon fluids shall be confined to their original strata until they can be produced and utilized without waste.

b. Rule 8a - Requires the protection of freshwater, whether above or below the surface, from pollution, whether in drilling, plugging, producing, or disposing of saltwater already produced.

c. Rule 8b - Requires that any oil or gas well, or well drilled for exploratory purposes, shall be drilled or operated in such a way that no pollution of any stream or water course, or any subsurface water will occur as the result of the escape or release or injection of oil, gas, saltwater, or other mineralized waters from any well.

d. Rule 8c - (Adopted April 3, 1967, effective January 1, 1969) Prohibits the use of saltwater disposal pits for storage and evaporation of oilfield brines and mineralized water; prohibits the discharge of oilfield brines and mineralized waters into a surface drainage water course; provides for the regulation of disposition of oilfield brines and mineralized waters generally.

e. Rule 8d - (Adopted May 1, 1969, and amended June 11, 1970) Prohibits the pollution of waters of the Texas offshore and adjacent estuarine zones (bays, inlets, and estuaries). The most recent amendment includes additional operations conducted on the Inland Fresh Waters of the State, such as lakes, rivers, and streams. This rule also sets minimum antipollution standards and practices which must be complied with during the drilling, production, and abandonment of such wells.

f. Rule 9 - Provides for the issuance of permits for saltwater disposal into disposal wells in nonproducing zones, and requires a letter of approval from the Texas Water Quality Board before such permits will be granted.

g. Rule 13 - Requires the operator of any well drilled, to set and cement a sufficient amount of surface casing to protect freshwater sands which are now or may be a source of water supply, and provides for acceptance of recommendations from the Texas Water Development Board as to the depth to which casing should be set for the adequate protection of freshwater.

h. Rule 13e - Provides for and sets minimum antipollution standards and practices which must be complied with during the cementing, drilling and completion, production, and abandonment of wells in Texas offshore waters (bays, inlets, and estuaries).

i. Rule 15 - Requires the protection of freshwater sands after the plugging of, or abandonment of, any well.

j. Rule 20 - Requires all operators to immediately notify the Commission by letter, giving full details concerning all fires, spills of oil, breaks, blowouts, or other losses of unrefined hydrocarbons. The reports are required to show the volume of crude oil, gas well liquids, or associated products lost. The location shall be identified by property name, survey, block, and county. Such reports must also specify what steps have been taken to remedy the situation.

k. Rule 71 (19)(a) - Requires all pipelines to report by telegraph, telephone, or letter, of each fire, break, or leak in any of its tanks or pipelines from which more than five (5) barrels oil is lost.

2. Special Field Rules

In most of the oil or gas fields of the State where special field rules have been adopted, the rules include requirements, in addition to the requirements of statewide rules, for the protection of freshwaters. In many fields special field rules also prohibit the use of earthen pits or other unacceptable surface disposal methods of oilfield brines.

3. Special Commission Orders

Special Orders issued by the Commission, such as those authorizing water or gas injection into a reservoir, include requirements for the adequate protection of both surface and subsurface freshwater supplies. Other special orders require the elimination of existing surface disposal installations for either fieldwide or areawide application.

Drilling Fluid Disposal

There has been some recent concern over the effects from the disposal of drilling fluids. Drilling mud disposal has been accomplished in Texas for many years by the following general methods without observing significant detrimental effects:

1. Inplace dehydration,
2. Utilization by landowners.
3. Reuses,
4. Central disposal system,
5. Subsurface disposal.

Our records of investigations have not shown that disposal of drilling fluid is a significant source of complaints. The disposal of such material is subject to the Commission's general rules that require any disposal operations not cause pollution.

DISCUSSION

MR. DENNIS G. WRIGHT (Environment Canada, Winnipeg, Manitoba, Canada): I think you are quite right in saying that we have not really observed any cases where there has been permanent long-term damage to the environment by the disposal of drilling wastes. But as an environmentalist, I have seen drilling fluids change from simple water to a gel system, to a weighted gel system, to an oil-base mud, and finally polymers. Right now, about 300 compounds in the world are used in the drilling of oil and gas wells. I just wonder, what is the next class of compounds that is going to be used in the drilling of wells, and exactly what effect is this going to have on the environment?

I realize that you do have to have a fluid to drill a well. And I realize that you are going to have waste produced and you have got to get rid of it some way. But let us be sure to do it the best way we can with the least amount of damage.

MR. SMITH: If anybody, any scientific group, shows the industry, and us, the regulatory agency, that there is a predictable problem, I do not think there would be any question that meaningful response to such a problem would occur.

CHAIRMAN FRITSCH: I would like to add to that question because this also applies to all the other fields of knowledge for which we have environmental concern.

Do we have to wait until something happens or do we wait for the collective mind to predict that something may happen? Shouldn't the burden of proof fall back to an industry that is making an awful lot of money on this and, also, on the regulatory agencies? Shouldn't we know what compounds go into the environment in the first place? We cannot wait until something harmful happens, can we?

MR. GEORGE H. HOLLIDAY (Shell Oil Company, Houston, Texas): I have sat here for 3 days engulfed in carcinogenic smoke. I think all of us recognize the proven correlation between lung cancer and the smoke; yet here you have a proven fact and nothing is done.

I cannot see why we keep looking ahead and trying to conjure conditions when we have conditions that we know are dangerous and nothing is done.

CHAIRMAN FRITSCH: I think that our government is doing something on the smoking question. When we ride the airplane home tonight or tomorrow, we will be able to sit in a smoking or nonsmoking section. Perhaps as regulations become more severe we may be riding in planes that will not have smoking at all in them.

The question that we raise here is a question that we would raise with your company, and with all others that are intervenors with the Environmental Protection Agency against my own organization. That is, we would like to know what is in gasoline. There are one or two Shell compounds involved there, too. We would like to know because the public has the right to know. I think the public's right to know is a major point here. We do not have to wait until something is proven wrong. We would like to know it beforehand. That is why a public corporation must answer some severe questions.

MR. HOLLIDAY: I am pleased to hear that comment, and I think it is very proper.

My only concern here is that you made a point a few minutes ago about our making a lot of money off of this. I submit, sir, that the Federal Government is reluctant to do anything about smoking because of the tax and of the income that results from that. It is in a position where it would lose revenue and that is more precious than the protection of the health.

MR. SMITH: The point that I raised is to look at documented cases. It was not to minimize the reasonable scientific searches into what potentially might happen. I just thought it would be somewhat pertinent to this discussion to look back at what has happened in history, in a State where we have drilled I have no idea how many thousands of wells, in just about all types of environments, with extensive development of underground water. It seems to me that the fact that we have not had specific problems in those areas with water wells 15 to 20 feet away from active drilling wells, is trying to tell us something.

So while you all are searching for that "what if" problem you might find what we have been doing right. Apparently, we have been doing something right because we haven't found these cases to occur naturally in the situations that we have investigated. And I just felt like that was an important point here because this has been our experience in investigating these problems.

DR. JOSEPH G. MONTALVO (Gulf South Research Institute, New Orleans, Louisiana): I would like to make one more comment.

I find that in listening to the people present at this conference over the past 3 days, a lot of us have got really excited about the potential effects when, in reality, if we really knew the detailed composition of the drilling muds and fluids, we could speak in more definitive terms. And I was quite surprised that very few of us who were the speakers here pointed out what would be the research needs of the field.

And I did that in my talk, if you remember, in that if we knew, for example, exactly what the trace elements were, and the species and the concentrations in these fluids, then we could have a better feel for saying whether or not we will have an environmental problem. But I do not think that it is fair or objective to criticize the people who make these chemicals and the industry using them when we do not really know what is contained in the fluids.

MR. HOLLIDAY: I have a couple of observations. I thought it was rather interesting, and I think along the lines of James Smith's comments, that all of the data and the observations relating to the environment show that little or no damage has resulted from our drilling with what has been classed, in many cases, as acutely toxic muds. The results by Tyson and Ray and Dr. George and Richard Zingula showed in the real life situation that damage is not occurring. I think that this is an important point, and certainly one, as I say, that James Smith made very well. I think both Dr. Louden and Mr. Smith made excellent points on land disposal when they talked about the abundant growth that seems to be prevalent with muds disposed of there.

Now, I'm a little confused with Mr. Wright's comment. I thought we were criticized awhile ago for looking only at components. All of a sudden I get the impression we are being criticized for not looking at components. We thought as a result we ought to be looking at hole muds. Now Environment Canada thinks we ought to go back to components. Is there any data available to show what we really need to look at or do we just each try pulling at the other end of the string until we finally break the string in the middle? And I think the break may turn out to be financial.

I think the data by Dr. Weir on whole mud is interesting--or Mr. Weir, perhaps--is very interesting, but it seems to me to be out of context as far as the real situation is concerned. A 50-50 mix of mud certainly does not tie very well to the dilution factors that Dr. Ray has shown for the marine environment.

Another comment I have concerns the discussion regarding the detoxification of mud as discussed with the Canadian disposal problem. It leaves me somewhat bewildered. First, I found in Mr. Shaw's comments no justification for the use of fish toxicology or toxicity criteria on dry land disposal of muds. Mr. Shaw's paper just sheds no light on this point at all. It was just evolved as axiomatic.

Secondly, the process appears rather strange to me. That is, we take what appears to be a harmless substance; we add a lot of unidentified chemicals to it, thereby increasing the concentration; we then take the liquid and throw it on the ground alongside the location, and take the concentrated material and bury it. This completely confuses me: to take what appears to be a perfectly valid material that could be used in farming; to take out all of the liquids and end up with a concentrate that could, indeed, be a problem; and then bury it so that it is exposed to the ground water. I am bewildered at the logic of that particular procedure.

In my opinion, spreading that mud on the ground makes better sense. And I am hoping that the work that Dr. Miller is proposing to do on this subject will, indeed, show the correctness of that particular position.

I note with some considerable interest that the data that has been presented here by industry, and the agencies, particularly Federal Government agencies, have been of considerable interest, except that I find that none of the agencies have put forth any hard data. There have been lots of "what-ifs," but to the best of my remembrance there has not been one paper that cited a condition that was bad or showed any hard laboratory or field data to support a problem.

The Canadians have looked at some materials. But in talking with Dr. Zitko, I find that he looked at a rather wild group of chemicals. Even he agrees that those particular chemicals are not necessarily those germane to drilling muds.

CHAIRMAN FRITSCH: If Dr. Zitko would have had a proprietary list, would you have looked at a little more specific list, Doctor?

DR. VLADIMIR ZITKO (St. Andrews, New Brunswick, Canada): Yes.

CHAIRMAN FRITSCH: The point is, here, I think, we have been playing a big game. You are talking a lot about hard data. I did not hear industry put out a lot of hard data either. I heard here that 200 of these compounds are proprietary and we cannot get our hands on them. What are we going to do about those 200? Could you tell us an answer to that?

MR. HOLLIDAY: How are you going to get a hold of 200 proprietary compounds? I think Dr. Zitko had, given by EPA, a very extensive list of compounds.

I want to address your point about no hard data. I thought the toxicological data that had been given by the mud companies was hard data. I thought the data given by Halliburton was outstandingly good on muds. And I rather resent the implication that we did not give data, particularly in view of the fact that I find no hard data from the agencies (and I ask the authors here from the agencies to speak, stand up and tell me what hard data they presented).

DR. WARREN C. MCMORDIE, JR. (Oil Base, Inc., Houston, Texas): There is no problem in getting proprietary information. All you have to do is ask.

CHAIRMAN FRITSCH: Well, you can ask.*

DR. MCMORDIE: And you can get it.

Let me say a little bit more about chemicals. I hear 200 and 400 and 600. There are not 200, 400, and 600. They may have been listed in the patent literature but they are not used. There are two dozen, fifty at the most, chemicals that are used in muds.

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*The above-mentioned file was sent to Dr. Fritsch in June. However, almost 90 percent of the names were tradenames and no indication of chemical formulas was given on these.

CHAIRMAN FRITSCH: Could we get a listing of the exact number with the amounts of those being used before we get our toxic substances bill, when we will be required by law to do such a thing?

MR. T. J. ROBICHAUX (Petrolite Corporation, St. Louis, Missouri): Warren, you might refer them back to the drilling fluids file, which for years has occurred annually in the Drilling and Production magazine. There is a total rundown of each drilling fluid additive by the company that produces it, by generic type of chemical that it is, and by the use for which it is intended. And I feel certain, although we do not produce any of them, that any manufacturer of those materials would be delighted to send you samples. We send samples of our materials to anybody that asks for them, except a competitor, and we have sent a few around to those.

But in the production chemicals, we are delighted to send samples, and I know that in the drilling fluids end they do the same thing.

DR. MCMORDIE: Well, certainly. On top of that, because of the OSHA requirements, all the toxicology data that we have available are listed. These data are not hidden.

MR. WRIGHT: I think it would be wise if the different manufacturers of the mud compounds got together and came up with one standard test against which they could screen all of the compounds.

Right now we have data, saying so and so has done such and such a test on such and such a compound. Somebody else may do a test on the same type of compounds, only using different organisms, different test conditions. How do you relate the two? So what I propose is to get together and come up with one simple test.

A PARTICIPANT: What would that test show?

MR. WRIGHT: Our philosophy is that we realize that each compound is going to be toxic in some degree. If you take the usage rate of that compound, and suppose the lethal concentrations which will kill 50 percent of your test organisms is a thousand parts per million, and then you look at exactly what is the concentration of that chemical in the mud system. If it is greater than a thousand parts per million, it is going to kill fish.

SEVERAL PARTICIPANTS: No.

A PARTICIPANT: Do you expect us to raise fish in the drilling mud?

MR. WRIGHT: No. I am expecting that when that stuff comes out of the pipe on an offshore operation, it is going to go into the environment and that chemical is going to be there.

A SPECTATOR: Is it going to be diluted?

MR. WRIGHT: Dilution of toxic materials should not be considered as an alternative to sound waste management practices, especially when sublethal effects of a toxicant are not known.

23 May 1975

Conference Summation

Farley Fisher, Ph.D.
General Chairman

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CONFERENCE SUMMATION

GENERAL CHAIRMAN FISHER: I would like to make a few acknowledgments. First, to Mr. Frank Ayer and his staff at the Research Triangle Institute for their work; to our session chairmen, Jim Lummus, Dr. Giam, Pat Wennekens, and Al Fritsch for their help and cooperation; to the army of you who spoke at this symposium. I certainly learned a lot from you and I hope everybody else here did the same. To a few people who were not quite apparent who were a great help to us and, in some respects, instrumental in bringing this program together, the Texas Mid-continent Oil and Gas Association, especially George Holliday and Frank Wheeler, and also the National Water Well Association and Jay Lehr; these people were extremely helpful to us in locating and corralling people to present papers here at this conference. And, also, to the Shamrock Hilton for their facilities and the help of their staff. And, finally, but perhaps most importantly, thanks to all of you who participated from the floor, raised a lot of questions and good points, and kept a lot of people honest. What we were trying to do is get a lot of things out and I think we have done that.

There are a few things which might be worth saying. I am in a job of trying to find where the bones are buried in the pollution business. I know that makes me very unpopular with a lot of people; they tend to look at me as kind of a prosecutor or witch hunter or something. But let me say that we have real environmental problems and we really do not have to go around inventing new ones.

I think we have had a lot of very good discussions here. I am inclined to agree that we did not really see any data that caused anyone immediate alarm. There were some if's and but's and maybe's. Maybe some of these need to be looked at further. I am not going to discuss them because I have to ruminate on them before I decide things like that. But on the whole, I think we are finding an industry which, at least, knows what good practice is. And I hope it is working hard to attain it. There seems to be a case to EPA for not butting in on this matter. The States and the Geological Survey, seem

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to be pretty much on top of this field, doing their best to regulate it. One has to wonder why we need another bull in the arena.

I was also struck by a couple of other things. One is that we have to avoid accepting simple answers to what are complex questions. And I must say, I am not sure what an LC_{50} on trout means in terms of environmental damage. I am not sure I would want to say anything regarding safety or danger on the basis of a test like that. Environmental harm is much more complex than killing a few trout. And I think that we cannot hope in the near future to invent a few very simple things that we can do and get a magic answer that says: "Yes, this is safe; no, this is not safe." We are going to have to take chances for a long time to come. And we are always going to have to watch what we do, especially when we start doing something new.

This, of course, is not an excuse for not being careful about the new things that we do, and not trying to reason ahead about what their implications might be. Which leads to another point; namely, that we must also remember that theory is no substitute for experiment and experience. The fruit of the pudding is in the eating. If the ground water is drinkable even after years and years of drilling in an area, there is a very good argument for the fact that the practices used in drilling were not upsetting the water.

However, we are drilling in new places all the time. And it is certainly true, as many of you have pointed out, that we are using new techniques all of the time. So the fact that we did things right 50 years ago does not mean that we are doing them right today. So we do have to be on the lookout and be on our guard.

I hope all of you have found this meeting as stimulating, as interesting, and as informative as I have. I want to thank you for your patience.

At this point I will throw the floor open for some general discussion if anybody wishes to make some closing comments.

MR. ROBERT B. ALLRED (Sun Oil Company, Richardson, Texas): Environmental Canada, I just want to point out one thing. I would not drink concentrated sodium hydroxide. I would not drink concentrated hydrochloric acid. However, if they were mixed together at the proper end-points, I would gladly drink them.

MR. DENNIS G. WRIGHT (Environment Canada, Winnepeg, Manitoba, Canada): Point taken. Granted, there are a lot of common everyday chemicals and things that occur naturally in the earth that are used in drilling fluids. But there are also an awful lot of synthetic materials that are used as well.

MR. ALLRED: But give them mixed together, do not give them individually. I do not use an individual mud. I use a mixture of things for the mud, not the individual products.

MR. WRIGHT: Right. But when you are looking at that, how can you separate the effects of a thinner or disperser, for example, from potassium chloride or caustic or something like that? You cannot do that in the hole mud. You have to do it individually.

MR. ALLRED: But the environment does not come in contact with lignosulfonate, for instance. The lignosulfonate goes into the clays and to the other chemicals. It is not sodium chromium lignosulfonate anymore. It has changed.

And as the good doctor pointed out, you put the pressure and heat in that oil well and you have got a good kettle for a lot of things that come out. And some of them, I might point out, may be worse than the individual materials themselves.

So look at it like it is. I just do not dump caustic in water; it is mixed in the mud.

GENERAL CHAIRMAN FISHER: I thank you. And this conference is now adjourned.

Comments Submitted After the Conference

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OBSERVATIONS AND REFLECTIONS ON THE CONFERENCE: ENVIRONMENTAL ASPECTS OF CHEMICAL USE IN WELL-DRILLING OPERATIONS

Dennis G. Wright*

I have had several days to reflect on the recent EPA-sponsored conference on the "Environmental Aspects of Chemical Use in Well-Drilling Operations", and would like to have the opportunity to voice my comments and concerns.

Although many excellent and informative papers were presented at the conference, I feel that more could have been gained had the Environment Canada/Department of Indian Affairs and Northern Development/Arctic Petroleum Operators Association Working Group had the opportunity to present more of the data garnered from our 2 years of studies related to drilling wastes in the Canadian North. The reports on the studies will be published in the fall of 1975 and can be obtained through our office.

I was distressed with some of the papers, especially the acute toxicity laboratory studies. It was apparent in some papers that there was only a rudimentary understanding of fish bioassay techniques. I would have liked to have seen data concerning the acute toxicity of some of the more exotic chemicals used in drilling fluids rather than data on weighting agents and gels. It has been our experience that some of these exotics are highly toxic and although their usage rate is low, there is the potential for sublethal effects and bioaccumulation. I believe that we should focus our attention on these chemicals in the near future.

The papers dealing with in situ field studies were very well presented. Although gross impairment of the ecosystem was not observed at any of the study sites, there were no detailed baseline data available on which to document subtle changes. If gross disturbance of a whole ecosystem is required before control measures are instituted, it is much too late. It is my opinion that controlled studies in the laboratory or

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*Biologist with the Fisheries and Marine Service, Environment Canada, Winnipeg, Manitoba, Canada.

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in a microcosm are necessary in order to detect the subtle changes occuring as a result of long-term waste discharges. I was disturbed that because no acute effects were observed in Timbalier Bay, it was assumed that there should not be any problems associated with the disposal of wastes to any aquatic or marine system--for instance, Lower Cook Inlet, the Beaufort Sea, or the interisland areas of the Canadian Arctic Archipelago. It must be emphasized that the Gulf of Mexico is a warm and diverse marine biological system, whereas the Beaufort Sea is clearly an Arctic marine environment about which we know very little. Disruptive effects must therefore be treated with caution.

During the course of the discussions I asked one of the speakers if there had been any observed changes in the structure of the shrimp community in the Gulf of Mexico. I was informed that none had been observed. I would like to draw your attention to a paper entitled "Impacts of Oil on the Gulf Coast" by L. S. St. Amant, presented at the 36th North American Wildlife and Natural Resources Conference, 1971, in which it was stated that a significant change in the shrimp population has occurred coincident to the rise of the offshore petroleum industry. Until the late 1940's and early 1950's, the white shrimp *Penaeus setiferus* made up 95 percent of the catch. In recent years, the population of brown shrimp *Penaeus aztecus* has increased to the point where this species frequently comprises more than 50 percent of the total catch. It is believed that this change has been induced by changes in the salinity of the estuarine nursery areas as a result of dredging and canaling by the petroleum industry. Although this phenomenon may not be related to the disposal of drilling fluids, it does point out that there has been an impact caused by the offshore industry. I might add that although the significance of the change in community structure is not understood, it nevertheless has occurred.

The fact that the industry representatives were not able to answer my question as to how much drilling fluid is disposed of from offshore operations is most distressing. Before any guidelines or regulations can be promulgated, there must be a clear understanding of the magnitude of the problem. It would seem logical to me that knowledge of the volumes disposed of is integral to the definition of the problem. It was our experience in the Canadian Arctic that operators were also unaware of the volume of fluids discharged. It has since been determined that using a combination of solids control equipment, the volume of discharge can be reduced to approximately 1.5 barrels of fluid per foot of hole. Improvements in solids control would be not only environmentally sound but economically sound as well.

Since the conference, our joint Industry/Government Working Group has completed the final draft of the guidelines for the disposal of drilling wastes in the Canadian North. As was stated at the conference, these guidelines are based on several simple points:

1) Reduction in the volumes of drilling fluids used through improvements in solids control systems;

2) Elimination of the more toxic drilling fluids components wherever possible;

3) Standardization of the testing of component chemicals;

4) Segregation of hydrocarbon-contaminated wastes;

5) Adjustment of pH to within the range of 6.0-9.5;

6) Dilution of wastes to at least 25:1 prior to discharge;

7) Elimination of waste discharge to freshwaters;

8) Construction, maintenance, and reclamation of reserve pits or sumps using best practical technology.

It is important to note that industry representatives comprised half of the working group and that these guidelines met with their approval.

It is my personal opinion that although a great deal of information was exchanged, the original objectives of the conference were not fully realized. I would have appreciated more information on trends in usage, new products likely to be introduced, and on the known environmental effects of a wider range of chemicals than was actually discussed. There are a great many questions still to be answered. The conference merely emphasized our lack of understanding of the problem. I hope that further research will be undertaken to resolve some of the questions posed.

I apologize to the conference for coming across as a radical; I was merely playing the role of "devil's advocate" in order to stimulate further discussion and thought on the topic.

I believe that much was gained by all as a result of the conference and that it accomplished many of its objectives. I would like to thank the conference coordinator for having created the forum in which I could voice my observations. Should you have any questions, please do not hesitate to ask.

REFERENCES

1. St. Amant, L. S., "Impact of Oil on the Gulf Coast," presented at 36th North American Wildlife and Natural Resources Conference, March 7-10, 1971, pp. 206-219.